

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A61L 9/00	A1	(11) International Publication Number: WO 97/25076 (43) International Publication Date: 17 July 1997 (17.07.97)
<p>(21) International Application Number: PCT/US97/00089</p> <p>(22) International Filing Date: 3 January 1997 (03.01.97)</p> <p>(30) Priority Data: 60/009,898 11 January 1996 (11.01.96) US 08/604,665 21 February 1996 (21.02.96) US</p> <p>(71) Applicant: ISK BIOSCIENCES CORPORATION [US/US]; 5966 Heisley Road, P.O. Box 8000, Mentor, OH 44061 (US).</p> <p>(72) Inventors: RAYTHATHA, Rasik, Haridas; 3618 Spring Arbor Way, Kingwood, TX 77345 (US). FOWLER, Randy, Eugene; 801 Briargreen Street, Pasadena, TX 77503 (US).</p> <p>(74) Agents: LEVY, Mark, P. et al.; 2000 Courthouse Plaza, N.E., P.O. Box 8801, Dayton, OH 45401-8801 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i> <i>With amended claims.</i></p>
<p>(54) Title: ODOR CONTROL FOR COMPOSITIONS CONTAINING ORGANIC SULFUR COMPOUNDS</p> <p>(57) Abstract</p> <p>A method and composition for controlling and reducing the odor of odoriferous components and/or by-products of formulations containing sulfur-containing organic compounds using a transition metal compound; the polyvalent transition metal compound is preferably provided on a carrier.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**ODOR CONTROL FOR COMPOSITIONS
CONTAINING ORGANIC SULFUR COMPOUNDS**

This application is claims the benefit of provisional application Ser. No. 60/009,898 filed Jan. 11, 1996.

Background of the Invention

The present invention relates to a method for controlling the odor of sulfur-containing organic compounds, such as nematicides and other pesticides, more particularly, this invention relates to a method for controlling the odor of sulfur-containing organic compounds using a polyvalent transition metal compound.

Agricultural compositions often include active agents which are sulfur-containing organic compounds which frequently exhibit odor. In many cases, the odor results from by-products and other impurities, such as low molecular weight mercaptans which are formed in the course of manufacturing the compounds. A number of approaches have been taken to controlling the odor of agricultural chemical formulations. Some of these approaches rely upon masking the odors with fragrances others have relied upon expensive methods, such as encapsulation. In general prior approaches have met with only limited success.

Japanese Patent No. 55/041846 to Furuya et al. discloses an adsorption process using activated charcoal impregnated with copper sulfate to remove the odorant, hydrogen sulfide, from a waste gas. Czechoslovakia Patent No. 175003 to Brych et al. teaches impregnation of common sorbents, such as activated charcoal, with metal salts to give a sorbent which traps ammonia, hydrogen sulfide and potassium cyanate gases at high relative humidity (greater than 75%). Japanese Patent No. 52/108388 to Hamaguchi discloses the treatment of activated charcoal-sodium pellets with metal ions for gas treatment or deodorization.

Adsorption by an activated charcoal carrier impregnated with a metal ion is not always an effective

approach to odor control because pesticides, such as Fosthiazate, bind to the activated charcoal so tenaciously that the Fosthiazate is not released and it is rendered nonfunctional as a pesticide.

Accordingly, there is a need for effective and cost efficient techniques for controlling and reducing the odor of sulfur-containing organic compounds, such as pesticides.

Summary of the Invention

It has been found that polyvalent transition metal compounds are useful in controlling and reducing the odor associated with sulfur-containing organic compounds. This finding is especially useful in controlling and reducing the odor of agricultural chemicals, such as pesticides. While the exact mechanism by which the transition metal compounds control the odor of the odoriferous components and by-products of the sulfur-containing organic compounds is not clear, the transition metal ions have been observed to complex with sulfur and it is believed that this complexation reaction may be functional in reducing odor in accordance with the present invention. The transition metal ions may complex with the odoriferous components and by-products. The transition metal ions may catalyze a reaction which decomposes the odoriferous components and by-products without affecting the stability of the sulfur-containing active agent. Furthermore, it is believed that the reaction is catalytic rather than adsorptive in nature because the odor control appears to endure indefinitely which suggests that the transition metal is not consumed in the reaction.

In accordance with one embodiment of the invention, the transition metal compound is simply added to a formulation containing a sulfur-containing organic compound. For example, a transition metal compound can be added neat to a solution or dispersion of an agricultural chemical which exhibits an odor problem. It does not appear to matter whether the transition metal compound dissolves in the formulation or not. The

transition metal compound has been observed to be capable of reducing odor if it dissolves in the formulation or if it simply resides as a sediment in the formulation.

The transition metal compound can also be dry mixed with a dry powder formulation and work effectively. While the transition metal compound can be used neat, it is preferred to adsorb or absorb or imbibe the transition metal compound onto an inert carrier. Where the formulation is a dry powder, a carrier containing the transition metal compound can be blended with the powder containing the active agent. In some cases, the active agent has been co-deposited on the carrier with the transition metal compound.

In summary, one manifestation of the present invention is for controlling the odor of odoriferous components and by-products of sulfur-containing organic compounds, such as nematicides and other pesticides, wherein a transition metal compound is added to the formulation containing the organic sulfur-containing compound.

Another manifestation of the invention is a composition useful in controlling the odor of sulfur-containing compounds which comprises a transition metal compound on a carrier and a sulfur-containing organic compound. In one particular embodiment of the invention, the composition comprises an inert carrier, a polyvalent transition metal compound and a sulfur-containing organic compound, such as a nematicide or other pesticide co-deposited on the carrier.

In another embodiment of the invention, the composition is a liquid formulation containing a sulfur-containing organic compound in which a polyvalent transition metal compound is dissolved or dispersed in the formulation.

In yet another embodiment of the invention, a container for a sulfur-containing organic compound which exhibits odor is provided wherein the container includes a compartment therein for retaining a polyvalent transition metal compound separate from, but in deodorizing communication with the sulfur-containing organic compound such that the odor

of the sulfur compound is reduced. The compartment is typically porous. Examples of porous elements that can be used with the invention are filter bags, perforated cap inserts, tubes of semi-permeable films, etc.

Still another embodiment of the invention is a carrier which is useful in controlling the odor of chemicals such as organic sulfur-containing compounds wherein the carrier has adsorbed or absorbed therein a transition metal compound.

Other objects and advantages of the present invention will be apparent from the following description and the appended claims.

Detailed Description

The use of polyvalent transition metal compounds in association with sulfur-containing organic compounds, such as nematocides and other pesticides, as described herein, provides unexpectedly good levels of odor control ranging from 24 hours to over one year. In addition to providing odor control, it has been observed that the polyvalent transition metal compounds provide enhanced stabilization of the active sulfur compounds in some cases. This stabilization has been observed using amounts less than is required for odor control. Throughout this disclosure, all references to sulfur containing organic compounds mean not only the active chemical but also the odoriferous components present with the active chemical to which the odor is generally attributed.

The polyvalent transition metal compound is preferably selected from a group consisting of copper, nickel, iron, zinc compounds and combinations thereof. Preferably, the polyvalent transition metal compound is a salt, such as a sulfate, nitrate or chloride. Representative examples of useful transition metal compounds include copper sulfate, nickel chloride, ferric chloride, zinc chloride, nickel sulfate, zinc sulfate, ferric sulfate and ferrous sulfate. More preferably, the salt is copper sulfate.

In accordance with the present invention, as previously noted, the transition metal compound can be associated with a sulfur-containing organic compound in various ways. In accordance with certain embodiments of the invention, the polyvalent transition metal compound is deposited onto an inert carrier. Any of a wide variety of inert carriers can be used for this purpose. Representative examples of useful carriers include clay granules, ground peanut hull, lava pumice stone, granulated gypsum, synthetic aluminum silicate, precipitated silica, activated charcoal, granular charcoal, powder kaolinite clays, granulated silica gel, powder silica, recycled paper granule, ground corncob, mullite, synthetic porous silicates, calcined clays, etc. More preferably, the inert carrier is selected from a group consisting of clay granules, ground peanut hull, lava pumice stone, granulated gypsum, synthetic aluminum silicate and precipitated silica. The carrier preferably has an average particle size in the range of about 18 to 50 mesh and a liquid holding capacity of about 0.15 to 3.5 ml water per gram carrier. However, those skilled in the art will recognize that carriers having a larger or smaller particle size and a higher or lower liquid holding capacity will also be useful.

Typically, the transition metal compound will be deposited on the carrier in an amount of about 0.01 to 15 parts compound per 100 parts carrier. The amount of the compound that can be added to the carrier will vary with the nature of the compound, the nature of the carrier and its particle size. When copper sulfate is used, the copper sulfate is added to the carrier in an amount ranging from 0.05 to 12% by weight of carrier.

The carrier can be impregnated with the transition metal compound using an aqueous imbibition technique. The transition metal compound is typically dissolved in an amount of water equal to about 40 to 95% of the liquid holding capacity of the inert carrier. After the carrier has taken up the solution of the transition metal compound, the carrier is

dried in a conventional manner. One useful method for drying the carrier is to use a fluidized bed dryer.

The amount of the polyvalent transition metal compound blended with the active sulfur containing compound is a function of several factors including the nature of the formulation and the manner in which the transition metal compound is used with the formulation, e.g., whether it is admixed dry, dispersed in a liquid, adsorbed on a carrier, or containerized, as described herein in more detail. Generally, the transition metal compound is added to the organic sulfur containing compound in an amount of about 0.02 to about 0.4 parts by weight per 100 parts by weight of the organic sulfur-containing compound (inclusive of its odoriferous contaminants or byproducts).

It is believed that polyvalent transition metal compounds should be effective in controlling the odor of substantially any sulfur-containing organic compound and be widely applicable in the field of agricultural chemicals. It is believed that the chemical entities responsible for the odor of these compositions react with the transition metal compound as previously discussed.

The sulfur-containing organic compound of the present invention is preferably selected from a group consisting of agricultural chemicals, such as pesticides. Representative examples of the agricultural chemicals include Fosthiazate, Chlormephos, Chlorpyrifos, methylene-bis-thiocyanate, Furadan and Thimate. The sulfur-containing organic compound can be in a granular or dry powder form or dispersion form. One of the advantages of the invention is that the addition of the odor control agent typically does not require a major change in the established formulation of the active agent.

In one embodiment of the invention, the active agent can be co-deposited on a carrier with the transition metal compound. The amount of the sulfur-containing organic compound deposited on the carrier will be a function of the EPA standards which regulate the application rate of the

compound. To deposit the sulfur-containing compound on the carrier, the sulfur-containing organic compound is dissolved in a solvent and the solution is sprayed upon or imbibed into the carrier. Substantially any solvent in which the sulfur-containing organic compound is soluble, which is easily removed by drying, and which does not attack the carrier, should be suitable for this purpose. A solvent useful for Fosthiazate is methylene chloride. The concentration of the solution is easily adjusted for the liquid holding capacity of the carrier to provide a product having the desired amount of the active agent on the carrier which can be applied to crops or soil in a conventional manner. The amounts of transition metal compound and sulfur-containing compound will be adjusted to provide the desired deodorizing effect. Generally, the transition metal compound is effective in relatively small amounts. Higher amounts can be used, provided that the amount of transition metal compound does not destabilize the active compound too greatly. Preferably, the transition metal compound is present in an amount of about 0.02 to 0.4 parts of the transition metal compound per 100 parts of the organic sulfur-containing compound as previously stated. For this embodiment wherein the transition metal compound and the active agent are co-deposited on the carrier, the transition metal compound is usually added to the carrier in an amount of about -0.025 to 0.25 parts by weight based on 100 parts by dry weight of the carrier alone.

In another embodiment, the composition is an admixture of a carrier containing a polyvalent transition metal compound and a dry powder formulation containing a sulfur-containing organic compound. In this embodiment, the transition metal compound is separately present on the carrier and mixed with the active compound in the amounts which have previously discussed.

In another embodiment, the composition is a liquid formulation containing the sulfur-containing organic compound in which a polyvalent transition metal compound is dissolved or dispersed. It is desirable that a surfactant is added to

the liquid formulation. The surfactant facilitates the blending of the formulation and the transition metal compound. Preferably, the transition metal compound is present in the liquid formulation in an amount ranging from about 0.2 to 14 parts by weight per 100 parts by weight of the organic sulfur containing compound.

Yet another embodiment of the present invention is a container for a liquid or powder formulation containing a sulfur-containing organic compound in which a compartment is provided for separately retaining a polyvalent transition metal compound. There must be vaporous communication between the compartment containing the transition metal compound and the formulation containing the sulfur compound. By associating the porous container containing the transition metal compound in proximity to the sulfur-containing organic compounds in this manner, the odoriferous components and by-products of the sulfur-containing organic compounds to come into contact with the transition metal compounds, thereby permitting deodorization. In this embodiment, the transition metal compound may be deposited onto a carrier in the same manner as described above or the compound may be used neat. The transition metal compound and carrier (optional) is then packaged in the compartment. The amount of transition metal compound that is packaged into the porous container is in the range from about 0.03 to 0.2 per 100 parts by weight of the organic sulfur containing compound.

Those skilled in the art will appreciate the diversity of materials that may be used to package the transition metal compound, such as a porous bag which may be paper or a microporous film formed into a bag which is simply added to the formulation, alternatively the transition metal compound can be housed in a cap or lid and separated from the formulation by a porous membrane of paper or film. A sponge member can be saturated with a solution of the transition metal compound, dried, and packaged with the formulation. The possible constructions are numerous.

The invention is illustrated in more detail by the following non-limiting examples.

In the following examples, odor is rated on a scale of 0 to 10, with 0 being no odor and 10 being extremely strong odor.

EXAMPLE 1

An inert carrier, 100 g granulated gypsum made by Agrisorbent Corporation (a division of Oil Dri Co.) with a maximum liquid holding capacity of 24 g of water/100 g of carrier, was impregnated with 0.2% by weight of copper sulfate pentahydrate supplied by Fisher Co., by dissolving 0.2 g of copper sulfate pentahydrate in 23 g of water and spraying this copper sulfate solution onto the carrier while gently mixing the granules. After all of the solution was added, the wet granules were mixed for 20 minutes using a device that tumbles granules with minimum shear force. The granules were then dried at 50°C in an oven for 8 hours. This pre-treated carrier was then treated with 10% of the sulfur-containing organic compound active ingredient, Fosthiazate. For loading, 8.93 g of carrier was used. 1.07 g of Fosthiazate was dissolved in 25 ml of methylene chloride. The solution of Fosthiazate was sprayed onto the carrier. Excessive amounts of methylene chloride were removed by vacuum evaporation.

EXAMPLE 2

The same carrier, polyvalent transition metal salt, active ingredient and method of preparing the carrier were used as in Example 1, except that the pre-treated carrier was loaded with Fosthiazate without using organic solvent. In this process Fosthiazate was sprayed directly on to carrier so there was no need to remove any solvent.

EXAMPLE 3

The type of carrier, transition metal compound and the method of impregnation were similar to Example 1.

However, the amount of transition metal compound was 0.05 g. Also, for final preparation 10.008 g of carrier impregnated with transition metal compound was used. In the process, 1.001 g of Fosthiazate was dissolved in 6 ml. of methylene chloride and added to the carrier. The rest of the process was similar to Example 1.

EXAMPLE 4

The type of carrier, transition metal compound and method of impregnation were similar to Example 1. However, the amount of transition metal compound was 0.05 g. Also, for final preparation 10.053 g of carrier impregnated with transition metal compound was used. In the process, 1.028 g Chlormephos was dissolved in 66.87 g of acetone and added to the carrier. The rest of the process was similar to Example 1.

EXAMPLE 5

The type of transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 1. However, the carrier was ground peanut-hull. The peanut-hull was ground to the size fraction between 18 to 30 mesh. The ground peanut-hull was dried overnight in an oven at 50°C. Separately, 0.026 g of transition metal compound was dissolved in 25.118 g of water and sprayed on to 12.48 g of the ground peanut-hull. The material was then dried overnight at 50°C to remove excessive moisture. The impregnation with Fosthiazate was carried out by dissolving 0.999 g of Fosthiazate in 6 ml. of methylene chloride. This solution was then added to 9.001 g of ground peanut-hull containing transition metal compound. The rest of the process was similar to Example 1.

EXAMPLE 6

The type of transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 1. However, the carrier was ground lava pumice stone from Guatemala. The carrier was in the size range of 12 to 35 mesh. As in Example 5, the carrier was dried overnight at 50°C. Separately, 0.078 g of transition metal compound was dissolved in 44.6 g of water, sprayed on to 100.2 g of the ground lava pumice stone, and dried overnight at 50°C. For Fosthiazate impregnation, the method and process were similar to Example 1.

EXAMPLE 7

The type of transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 1. However, the carrier was Synthetic Silica BXR 493 supplied by PPG Industries, Inc. The carrier was in the size range of 35 to 120 mesh. As in Example 5, the carrier was dried overnight at 50°C. Separately, 0.008 g of transition metal compound was dissolved in 102.3 g of water, sprayed on to 30.02 g of the carrier, and dried overnight at 50°C. For Fosthiazate impregnation, the method and process were similar to Example 1.

EXAMPLE 8

The type of transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 1. However, the carrier was Agsorb CN, manufactured by Agrisorbents (Group of Oil Dri). The carrier was in the size range of 24 to 48 mesh. As in Example 5, the carrier was dried overnight at 50°C. The amount of carrier used ranged from 100.000 g to 99.755 g. Various amounts of transition metal compound ranging from 0.000 g to 0.258 g was dissolved in 0 g to 20.003 g of water and sprayed on to the carrier. For Fosthiazate impregnation, the method and process were similar to Example 1.

EXAMPLE 9

A liquid formulation was prepared by dissolving 0.15 g copper sulfate in 161.67 g of water. To increase wetting and dispersing of the organic sulfur compound, 9.0 g of a surfactant was added to the liquid formulation. The organic sulfur compound, Methylene-bis-thiocyanate, was added to the formulation in an amount of 45.62 g. In addition, 45.62 g of another non-sulfurous active ingredient, Chlorothalonil, was also added to the formulation. This formulation was ground using a ball mill and its viscosity was adjusted. The resulting suspension concentrate had an odor rating of 3 compared to an odor rating of 10 for similar formulations prepared without copper sulfate.

EXAMPLE 10

A carrier, 10 g activated charcoal, was impregnated with a polyvalent transition metal compound, 10% by weight of carrier CuSO_4 . The pre-treated carrier was then packaged into a small filter bag in an amount of 0.3 g. This bag was then left in a container containing 10 g of a Fosthiazate formulation. Three observers were asked to rate severity of the odor on the scale of 0 to 10 where 0 indicates total odor control and 10 means no odor control. Use of the deodorizer gave odor control of 3 or less.

EXAMPLE 11

The type of polyvalent transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 10. However, the carrier was Kurry charcoal from Japan. The carrier was dried overnight at 50°C before using. 163.7 g of copper sulfate was dissolved in 950 g of water and sprayed on to 1200.2 g of dried Kurry charcoal. The resulting material was once again dried overnight at 50°C. 0.1 g, 0.2 g and 0.3 g of the resulting material was packaged in small micro-porous filter bags. These bags were then placed in containers containing 10 g of Fosthiazate 10G formulation. The odor was rated at regular intervals after

storage at ambient condition and at 45°C. Table I below shows that the copper sulfate impregnated Kurry charcoal produced a significant reduction in the odor. The results are based on an average of three observations.

TABLE I

COPPER KURRY CHAR- COAL	ODOR RATING AT AMBIENT CONDITIONS AND 45°C FOR DAYS											
	<u>2</u>		<u>3</u>		<u>6</u>		<u>17</u>		<u>38</u>		<u>48</u>	
	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>
0.0	10	10	10	10	10	10	10	10	10	10	10	10
0.1	1	1	1	1	2	2	0	0	2	1	0	1
0.2	1	0	1	0	1	1	0	0	0	1	1	1
0.3	0	0	0	1	0	1	0	0	0	1	0	1

EXAMPLE 12

The type of polyvalent transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 10. However, the carrier was calcined Kaolinite, Alphatex supplied by ECC America. The carrier was dried overnight at 50°C before using. 10 g of copper sulfate was dissolved in 45 g of water and sprayed on to 90 g of dried Alphatex. The resulting material was once again dried overnight at 50°C. 0.1 g, 0.2 g and 0.3 g of the resulting material was packaged in small micro-porous filter bags. These bags were placed in containers containing 10 g of Fosthiazate 10G formulation. The odor was rated at regular intervals after storage at ambient and at 45°C. Table II below shows that the copper sulfate impregnated Alphatex produced a significant reduction in the odor. The results are based on an average of three observations.

TABLE II

COPPER

KURRY

ODOR RATING AT AMBIENT CONDITIONS AND 45°C FOR DAYS

CHAR-

COAL

	<u>2</u>		<u>3</u>		<u>6</u>		<u>17</u>		<u>38</u>		<u>48</u>	
	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>
0.0	10	10	10	10	10	10	10	10	10	10	10	10
0.1	6	5	7	6	6	8	2	4	4	5	2	3
0.2	2	2	5	1	4	4	1	1	3	4	1	4
0.3	3	1	3	1	3	3	1	1	2	3	1	3

EXAMPLE 13

The type of polyvalent transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 10. However, the carrier was precipitated silica. The silica was precipitated by acidification of sodium silicate with sulfuric acid. The precipitated silica was washed thoroughly to remove adsorbed salt and dried in oven at 50°C. The material was ground and particles below 100 mesh were collected. 0.026 g of copper sulfate was dissolved in 6.013 g of water and sprayed on to 12.493 g of dried precipitated silica. The resulting material was then dried at 50°C for 24 hours to remove excess water. 0.023 g of nickel chloride was dissolved in 6.034 g of water and sprayed on to 12.494 g of dried precipitated silica. The resulting material was then dried at 50°C to remove excess water. Fosthiazate was impregnated on to these resulting materials as in Example 10. Table III below shows that copper sulfate and nickel chloride impregnated carriers produce a significant reduction in odor.

TABLE III

<u>DEODORIZER</u>	<u>ODOR RATING AT AMBIENT CONDITIONS OR 45°C.</u>		
	<u>2 DAYS @ AMB</u> <u>CONDITIONS</u>	<u>6 MONTHS @ AMB</u> <u>CONDITIONS</u>	<u>6 MONTHS @</u> <u>45°C</u>
None	10	10	10
Silica w/ copper	0	5	3
Silica w/ nickel	2	4	4

EXAMPLE 14

The type of polyvalent transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 10. However, the carrier was dried Kurry charcoal. The amount of copper sulfate was in the range of 0.2 to 12% by weight of carrier. The amount of copper sulfate was varied as follows: 1) 163.7 g of copper sulfate was dissolved in 950 g of water and sprayed on to 1200.2 g of Kurry charcoal granules. The resulting material was dried overnight at 50°C. The resulting material had a copper sulfate loading of 11.95%; 2) for medium loading material, 18.05 g of copper sulfate was dissolved in 144.1 g of water and sprayed on to 182.02 g of Kurry charcoal. The resulting material was dried overnight at 50°C. The resulting material had a copper sulfate loading of 9.0%; 3) for lower loading material, 3.6 g of copper sulfate was dissolved in 960 g of water and sprayed on to 1200 g of Kurry charcoal. The resulting material was dried overnight at 50°C. The resulting material had a copper sulfate loading of 0.3%. 0.2 g of each of the resulting materials was packaged in micro-porous filter bags and placed with 20 g of Fosthiazate granules. The odor was rated after 24 hour day and one week. Table IV below shows that the loading percent of copper sulfate on to a carrier does not have a significant effect on the reduction in odor.

TABLE IV

LOADING OF COPPER SULFATE (%)	ODOR RATING	
	@ 24 HOURS	@ 1 WEEK
0.3	1	2
9.0	1	1
11.95	1	1

EXAMPLE 15

The type of active ingredient and method of impregnating the carrier were similar to Example 10. However, the carrier was precipitated silica and the transition metal compounds were nickel chloride hexahydrate and ferric (III) chloride hexahydrate. 0.115 g of nickel chloride hexahydrate was dissolved in 9.6 g of water and sprayed on to 15 g of silica. The resulting material was dried at 50°C for 24 hours. 0.128 g of ferric (III) chloride hexahydrate was dissolved in 9.6 g of water and sprayed on to 15 g. of silica. The resulting material was dried at 50°C for 24 hours. 0.3 g of the resulting materials were packaged in filter bags and placed in contact with 50 g of Fosthiazate granules. The odor was rated after 2, 3 and 8 days. Table V below shows that the nickel chloride produced a more significant reduction in odor.

TABLE V

TRANSITION METAL COMPOUND	ODOR RATING		
	2 DAYS	5 DAYS	8 DAYS
Nickel chloride	1	1	0
Ferric chloride	3	2	1

EXAMPLE 18

The type of active ingredient and method of impregnating the carrier were similar to Example 10. However, the carriers for this study were precipitated silica and Kurry charcoal and the transition metal compounds were copper sulfate and nickel chloride. Both carriers were dried at 50°C for 24 hours before transition metal compound impregnation. 0.121 g. of copper sulfate pentahydrate was dissolved in 9.6 g of water and sprayed on to 15 g of dry silica. The resulting material was dried at 50°C for 24 hours. 0.115 g of nickel chloride hexahydrate was dissolved in 9.6 g of water and sprayed on to 15 g of dry silica. The resulting material was dried at 50°C for 24 hours. 3.6 g of copper sulfate was dissolved in 960 g of water and sprayed on to 1200 g of Kurry charcoal. The resulting material was dried overnight. The resulting material had a loading of 0.3% copper sulfate. 0.05 g of each resulting material was placed directly into contact with 2.0 g of Fosthiazate 75% EC. The odor was rated after 1, 24 and 144 hours. Table VI below shows that the nickel chloride generally produced a more significant reduction in odor.

TABLE VI

<u>CARRIER</u>	<u>ODOR RATING AFTER STORAGE FOR PERIOD OF TIME</u>		
	<u>1 HOUR</u>	<u>24 HOURS</u>	<u>144 HOURS</u>
Copper/Kurry	8	4	3
Copper/Silica	3	8	8
Nickel/Silica	6	3	3

EXAMPLE 19

The carrier was Agsorb S2100CN supplied by Agrisorbents (Oil Dri) Europe. The carrier was in the size range of 24 to 48 mesh. The carrier was dried overnight at 50°C. The transition metal compound is copper sulfate. 0.008 g of copper sulfate was dissolved in 7.2 g of water and

sprayed on to 30.0 g of Agsorb S2100CN. The resulting material was dried overnight at 50°C. For Fosthiazate impregnation method and process were similar to Example 1. The odor was rated after one week and one month of storage at 22°C and at 45°C. Table VII below shows that the copper sulfate on this carrier produced a significant reduction in odor. The results are based on an average of three observations.

TABLE VII

<u>CARRIER</u>	<u>% COPPER SULFATE</u>	<u>ODOR RATING AFTER 1 WEEK</u>		<u>ODOR RATING AFTER 1 MONTH</u>	
		<u>22°C</u>	<u>45°C</u>	<u>22°C</u>	<u>45°C</u>
Agsorb S2100CN	0.00	9	10	10	10
Agsorb S2100CN	0.025	1	2	1	1

EXAMPLE 20

The carrier was Biofix E2 supplied by ECC International. The carrier was in the size range of 24 to 48 mesh. The carrier was dried overnight at 50°C. The transition metal compound is copper sulfate. 0.008 g of copper sulfate was dissolved in 9.2 g of water and sprayed on to 30.022 g of Biofix E2. The resulting material was dried overnight at 50°C. For Fosthiazate impregnation method and process were similar to Example 1. The odor was rated after one week and one month of storage at 22°C and at 45°C. Table VIII below shows that the copper sulfate on this carrier produced a significant reduction in odor. The results are based on an average of three observations.

TABLE VIII

<u>CARRIER</u>	<u>% COPPER SULFATE</u>	<u>ODOR RATING AFTER 1 WEEK</u>		<u>ODOR RATING AFTER 1 MONTH</u>	
		<u>22°C</u>	<u>45°C</u>	<u>22°C</u>	<u>45°C</u>
Biofix E2	0.00	9	10	10	10
Biofix E2	0.025	2	1	2	2

EXAMPLE 21

The carrier was Illite clay granules supplied by Kentish Mineral. The carrier was in the size range of 18/40 mesh. The carrier was dried overnight at 50°C. The transition metal compound is copper sulfate. 0.008 g of copper sulfate was dissolved in 8.5 g of water and sprayed on to 30.004 g of Illite clay granules. The resulting material was dried overnight at 50°C. For Fosthiazate impregnation method and process were similar to Example 1. The odor was rated after one week and one month of storage at 22°C and at 45°C. Table IX below shows that the copper sulfate on this carrier produced a significant reduction in odor. The results are based on an average of three observations.

TABLE IX

<u>CARRIER</u>	<u>% COPPER SULFATE</u>	<u>ODOR RATING AFTER 1 WEEK</u>		<u>ODOR RATING AFTER 1 MONTH</u>	
		<u>22°C</u>	<u>45°C</u>	<u>22°C</u>	<u>45°C</u>
Illite 18/40	0.00	9	10	10	10
Illite 18/40	0.025	1	2	2	2

EXAMPLE 22

The carrier was Biodac (recycled paper) granules supplied by Edward Lowe Industry. The carrier was in the size range of 16/30 mesh. The carrier was dried overnight at 50°C. The transition metal compound is copper sulfate. 0.008 g of copper sulfate was dissolved in 13.6 g of water and sprayed on to 30.004 g of Biodac granules. The resulting material was dried overnight at 50°C. For Fosthiazate impregnation method and process were similar to Example 1. The odor was rated after one week and one month of storage at 22°C and at 45°C. Table X below shows that the copper sulfate on this carrier produced a significant reduction in odor. The results are based on an average of three observations.

TABLE X

<u>CARRIER</u>	<u>% COPPER SULFATE</u>	<u>ODOR RATING AFTER</u> <u>1 WEEK</u>		<u>ODOR RATING AFTER</u> <u>1 MONTH</u>	
		<u>22°C</u>	<u>45°C</u>	<u>22°C</u>	<u>45°C</u>
Biodac 16/30	0.00	9	10	10	10
Biodac 16/30	0.025	1	2	1	2

EXAMPLE 23

Four 10 g samples of Agsorb CN carrier supplied by Agrisorbents product group (A division of Oil Dri Corporation of America) were impregnated with 0.05%, 0.10%, 0.20% and 0.25% CuSO₄, respectively. The carriers were then impregnated with Fosthiazate and stored for 12 months at 22°C and 45°C. Fosthiazate impregnation was accomplished by dissolving 1.0 g of Fosthiazate in 6 ml. of methylene chloride. The resulting solution was blended with the carrier for 15 minutes. Volatile methylene chloride was removed by vacuum using Büchi rotovaporizer. The impregnated carriers were evaluated as to their odor compared with a 10 g Agsorb CN carrier impregnated with only Fosthiazate, no CuSO₄. Table XI below shows that the

odor rating of the carriers with CuSO_4 is substantially less than that of the carrier without CuSO_4 .

TABLE XI

<u>TEMP.</u>	<u>ODOR RATING</u>				
	0.0% <u>CuSO_4</u>	0.05% <u>CuSO_4</u>	0.10% <u>CuSO_4</u>	0.20% <u>CuSO_4</u>	0.25% <u>CuSO_4</u>
22°C	10	2	1	1	1
45°C	10	1	0	0	0

EXAMPLE 24

Two groups of four carriers were impregnated with Fosthiazate and stored for 6 months at 22°C and 45°C to evaluate the odor. The four carriers were: 1) Mexican pumice stone, 2) Mexican pumice stone impregnated with 0.05% CuSO_4 , 3) Guatemalan pumice stone, 4) Guatemalan pumice stone impregnated with 0.05% CuSO_4 . Table XII below shows that the odor rating of the carriers that were impregnated with CuSO_4 were substantially less than the carriers without CuSO_4 , especially at the storage temperature of 45°C.

TABLE XII

<u>STORAGE</u> <u>TEMP.</u>	<u>ODOR RATING</u>			
	<u>MEXICAN</u>	<u>MEXICAN/</u> <u>CuSO_4</u>	<u>GUATEMALAN</u>	<u>GUATEMALAN/</u> <u>CuSO_4</u>
22°C	2	2	6	2
45°C	8	1	6	1

EXAMPLE 25

Two groups of four Agsorb CN carriers were impregnated with Fosthiazate after being impregnated with different amounts of CuSO_4 to evaluate the effect of CuSO_4 concentration on odor. One group of impregnated carriers were stored for 55 days at room temperature and the other was stored for 55 days at 45°C. Table XIII below shows that the odor rating substantially decreases with the addition of CuSO_4 .

TABLE XIII

STORAGE 55 DAYS (TEMP.)	ODOR RATING				
	0.0% <u>CuSO_4</u>	0.05% <u>CuSO_4</u>	0.10% <u>CuSO_4</u>	0.20% <u>CuSO_4</u>	0.25% <u>CuSO_4</u>
R.T.	10.0	2.0	1.0	0.0	0.0
45°C	10.0	1.0	2.0	0.0	0.0

EXAMPLE 26

Two samples of 0.3 g of charcoal carrier were impregnated with CuSO_4 and then packaged into micro-porous filter bags (similar to tea bags) and stowed inside perforated bottle caps. The bottle caps were then used to close containers containing Fosthiazate. The combinations were stored at room temperature and at 45°C for various periods to evaluate the effect of charcoal impregnated with CuSO_4 on the odor rating. Table XIV below shows that there is an immediate decrease in the odor and a continued odor controlling effect.

TABLE XIV

<u>DAYS OF STORAGE</u>	<u>ODOR RATING</u>	
	<u>AT ROOM TEMP.</u>	<u>AT 45°C</u>
0	10	10
1	1	1
2	0	0
3	0	1
5	0	1
18	0	0
48	0	1
116	0	1

EXAMPLE 27

Six different types of deodorizers were placed within containers containing Fosthiazate 75% EC. The deodorizers were in direct contact with the Fosthiazate. The containers were stored at room temperature for various lengths of time. The amount of deodorizer packaged into the porous container was varied. Table XV below shows that carriers impregnated with polyvalent transition metal compounds gave the best odor control, even at lower concentrations. However, Cu/Silica was not very effective for longer periods.

TABLE XV

<u>DEODORIZER</u>	<u>PERCENT</u> <u>DEODORIZER</u>	<u>ODOR RATING AT ROOM TEMPERATURE</u>			
		<u>1 HR</u>	<u>24 HRS</u>	<u>30 DAYS</u>	<u>5 MONTHS</u>
None	0.0	10.0	10.0	10.0	10.0
Epoleon N-100	1.0	10.0	10.0	10.0	10.0
Epoleon NnZ	1.0	10.0	10.0	10.0	10.0
Epoleon N7C	1.0	10.0	10.0	10.0	10.0
Cu/Charcoal	0.5	8.0	4.0	2.0	N/A
Cu/Silica	0.5	3.0	8.0	8.0	8.0
Ni/Silica	0.5	6.0	3.0	2.0	2.0

EXAMPLE 28

A comparison of the types of odor eliminators was conducted. The control was no odor eliminator. The odor eliminators were charcoal, 0.3 g charcoal impregnated with copper and 0.3 g clay impregnated with copper. The deodorizers were packaged into micro-porous filter bags placed directly over 20.0 g of Fosthiazate granules contained within a container and stored for 14 days at room temperature and at 45°C and for 439 days at room temperature and at 45°C. The odor control of each type of deodorizer was evaluated. Table XVI below shows that the charcoal impregnated with copper gave the best odor control.

TABLE XVI

STORAGE DAYS AT TEMP.	ODOR RATING			
	<u>CONTROL</u>	<u>CHARCOAL</u>	<u>Cu/CHARCOAL</u>	<u>Cu/CLAY</u>
14 Days/ Room Temp.	10	3	0	1
14 Days/ 45°C	10	4	0	1
439 Days/ Room Temp.	10	6	1	1
439 Days/ 45°C	10	7	0	1

EXAMPLE 29

A comparison of the types of odor eliminators was conducted. The control was no odor eliminator. The odor eliminators were charcoal, charcoal impregnated with copper and clay impregnated with copper. 0.1 g of each deodorizer was packaged into a micro-filter bags placed directly over 20.0 g of Fosthiazate granules contained within a container and stored at room temperature for various days. The odor control of each deodorizer was evaluated. Table XVII below shows that the activated charcoal impregnated with copper gave the best odor control. Clay impregnated with copper was less effective at controlling odor. Activated charcoal was only partially effective in controlling odor over a 120 day period.

TABLE XVII

<u>DAYS OF STORAGE</u>	<u>ODOR RATING</u>			
	<u>CONTROL</u>	<u>CHARCOAL</u>	<u>Cu/CHARCOAL</u>	<u>Cu/CLAY</u>
0	10	10	10	10
1	10	8	2	7
5	10	5	1	6
10	10	4	2	6
20	10	6	0	2
50	10	8	0	2
110	10	8	1	3
440	10	8	1	4

EXAMPLE 30

Various amounts of charcoal impregnated with copper were packaged into micro-porous filter bags and placed directly over 20 g of Fosthiazate 10G granules contained within a container. The containers were stored for various lengths of time at room temperature to evaluate the effect of deodorizer concentration on odor control. Table XVIII below shows that all the amounts of Cu/Charcoal were effective in controlling odor.

TABLE XVIII

<u>DAYS OF STORAGE</u>	<u>ODOR RATING AT VARIOUS AMOUNTS OF DEODORIZER</u>			
	<u>0.0 g</u>	<u>0.1 g</u>	<u>0.2 g</u>	<u>0.3 g</u>
0	10	10	10	10
5	10	1	1	0
10	10	1	1	0
20	10	0	0	0
440	10	1	1	1

EXAMPLE 31

A comparison of the types of odor eliminators was conducted. The control was no odor eliminator. The odor eliminators were charcoal, charcoal impregnated with copper and clay impregnated with copper. 0.1 g of each deodorizer was packaged into micro-porous filter bags and placed directly over 20.0 g of Fosthiazate granules contained within a container and stored at 45°C for various days. Table XIX below shows that the charcoal impregnated with copper gave the best odor control.

TABLE XIX

<u>DAYS OF STORAGE</u>	<u>ODOR RATING</u>			
	<u>CONTROL</u>	<u>CHARCOAL</u>	<u>Cu/CHARCOAL</u>	<u>Cu/CLAY</u>
0	10	10	10	10
1	10	8	2	6
2	10	6	1	5
4	10	5	0	6
6	10	6	1	8
18	10	7	0	4
45	10	5	1	3
116	10	6	3	5

EXAMPLE 32

0.3 g and 0.6 g of charcoal carrier were impregnated with copper and packaged into micro-porous filter bags and placed directly over various amounts of Fosthiazate granules contained within containers and stored for 370 days at room temperature and 45°C to evaluate the effect of the amount of Fosthiazate on the odor control of the carrier. The control was no deodorizer. Table XX below shows that the amount of Fosthiazate does not significantly alter the odor controlling properties of the carriers, especially when a larger amount of carrier is used.

TABLE XX

STORAGE TEMP. AND DEODORIZER		ODOR RATING BASED ON AMOUNT OF <u>FOSTHIAZATE IN GRAMS</u>				
		<u>50</u>	<u>95</u>	<u>145</u>	<u>295</u>	<u>395</u>
ROOM TEMP.	Control	10	10	10	10	10
	0.3 g Cu/Charcoal	1	3	4	5	5
	0.6 g Cu/Charcoal	0	2	2	4	2
	45°C Control	10	10	10	10	10
	0.3 g Cu/Charcoal	3	3	3	5	7
	0.6 g Cu/Charcoal	3	2	3	3	3

EXAMPLE 33

Various amounts of charcoal impregnated with copper were packaged into micro-porous filter bags and placed directly over 20 g of Fosthiazate 10G contained within containers. The containers were stored for various lengths of time at room temperature to evaluate the effect of deodorizer concentration on odor control. Table XXI below shows that all the amounts of Cu/Charcoal were effective in controlling odor.

TABLE XXI

<u>DAYS OF STORAGE</u>	<u>ODOR RATING AT VARIOUS AMOUNTS OF DEODORIZER</u>			
	<u>0.0 g</u>	<u>0.1 g</u>	<u>0.2 g</u>	<u>0.3 g</u>
0	10	10	10	10
1	10	1	1	0
2	10	1	1	0
7	10	1	1	0
14	10	0	0	0

EXAMPLE 34

0.3 g and 0.6 g of charcoal carrier were impregnated with copper and packaged into micro-porous filter bags and placed directly over various amounts of Fosthiazate granules contained within containers and stored for 8 days at room temperature to evaluate the effect of the amount of Fosthiazate on the odor control of the carrier. The control was no deodorizer. Table XXII below shows that the impregnated carriers were effective for a wide range of amounts of Fosthiazate.

TABLE XXII

<u>CARRIER</u>	<u>ODOR RATING BASED ON AMOUNT OF FOSTHIAZATE IN GRAMS</u>				
	<u>50</u>	<u>95</u>	<u>145</u>	<u>295</u>	<u>395</u>
Control	10	10	10	10	10
0.3 g Cu/Charcoal	2	3	4	6	8
0.6 g Cu/Charcoal	1	1	1	2	2

EXAMPLE 35

25 g emulsifiable concentrate of Fosthiazate was contained in a container with a cap that housed a compartment filled with 1.0% charcoal carrier impregnated with copper to evaluate the odor controlling effect of the Cu/Charcoal. Table XXIII below shows that the Cu/Charcoal significantly reduces the odor of the emulsifiable concentrate.

TABLE XXIII

STORAGE DAYS	ODOR RATING	
	75% EC (CONTROL)	75% EC + 1.0% Cu/CHARCOAL
0	10	10
7	10	5
22	10	3
34	10	3

In addition to the odor control, the polyvalent transition metal compounds also enhance the stability of the sulfur-containing organic compounds impregnated into a polyvalent transition metal compound treated carrier. Several tests which follow were completed to support this finding.

EXAMPLE 36

Two Fosthiazate impregnated carriers were prepared. The first carrier, acidic peanutshell, was impregnated only with the Fosthiazate. The second carrier, acidic peanutshell, was impregnated first with CuSO₄ and then with Fosthiazate. Table XXIV below shows the results of the study that evaluated the stability of Fosthiazate. The stability of Fosthiazate is significantly enhanced when a carrier is pre-treated with a polyvalent transition metal compound.

TABLE XXIV

<u>TIME AND TEMP.</u>	<u>% FOSTHIAZATE ON ACIDIC PEANUTSHELL</u>	<u>% FOSTHIAZATE ON COPPER/PEANUTSHELL</u>
Initial	9.90	10.1
One week @ 45°C	9.60	N/A
One month @ 45°C	3.50	N/A
2 months @ Rm.Temp	N/A	10.0
2 months @ 45°C	N/A	9.40

EXAMPLE 37

Four Fosthiazate impregnated carriers were prepared and stored at 22°C for 0 to 180 days to evaluate the percent of Fosthiazate remaining in the carriers. The first carrier was Mexican pumice stone. The second carrier was Mexican pumice stone impregnated with 0.05% by weight carrier CuSO_4 . The third carrier was Guatemalan pumice stone. The fourth carrier was Guatemalan pumice stone impregnated with 0.05% by weight carrier CuSO_4 . Table XXV below shows that only a minute percent of Fosthiazate is lost during the 180 days of storage.

TABLE XXV

<u>DAYS OF STORAGE</u>	<u>% FOSTHIAZATE REMAINING ON CARRIER</u>			
	<u>MEXICAN CARRIER</u>	<u>MEXICAN & CuSO₄</u>	<u>GUATEMALAN CARRIER</u>	<u>GUATEMALAN & CuSO₄</u>
0	9.8	9.9	10.5	11.3
60	9.6	10.6	11.1	11.4
180	9.7	9.6	10.5	11.3

EXAMPLE 38

Four 10G Agsorb CN carriers were impregnated with 0.05%, 0.10%, 0.20% and 0.25% CuSO_4 , respectively. The carriers were then impregnated with 10.3% Fosthiazate and stored for 370 days to evaluate the effect of CuSO_4 concentration on the stability of the Fosthiazate. Table XXVI

below shows that lower concentrations of CuSO₄ stabilize the Fosthiazate better than higher concentrations.

TABLE XXVI

<u>DAYS OF STORAGE</u>	<u>% FOSTHIAZATE REMAINING ON CARRIER</u>			
	<u>0.05% CuSO₄</u>	<u>0.10% CuSO₄</u>	<u>0.20% CuSO₄</u>	<u>0.25% CuSO₄</u>
0	10.5	10.5	10.5	10.5
50	9.6	10.0	10.0	10.0
180	10.3	11.0	10.2	9.8
370	10.2	9.8	9.6	6.0

EXAMPLE 39

Two groups of four different types of carriers were impregnated with 0.025% CuSO₄ and different amounts of Fosthiazate and stored for 6 weeks at 22°C and 43°C to evaluate the effect of various carriers on stability. The carriers were: Agsorb CN, Mexican pumice stone, Guatemalan pumice stone, and Costa Rica pumice stone. Table XXVII below shows that the Guatemalan pumice stone carrier gave the best stability.

TABLE XXVII

<u>WEEKS & STORAGE TEMP.</u>	<u>% FOSTHIAZATE REMAINING ON CARRIER</u>			
	<u>AGSORB CN</u>	<u>MEXICAN</u>	<u>GUATEMALAN</u>	<u>COSTA RICA</u>
Initial	10.8	8.8	8.2	9.5
6 Wks/22°C	10.1	9.4	10.8	9.3
6 Wks/43°C	9.3	8.1	11.5	8.5

EXAMPLE 40

An Agsorb CN carrier was impregnated with 0.05% nickel ion. Two peanutshell carriers were impregnated with 0.025% copper ion and 0.025% nickel ion, respectively. A pumice stone carrier was not impregnated with a metal ion. All the carriers were impregnated with Fosthiazate and stored at 22°C for up to 150 days to evaluate the effect of carriers and metal ions on the stability of Fosthiazate. Table XXVIII below shows that peanutshell carrier impregnated with nickel ion stabilized the Fosthiazate the best after 150 days of storage.

TABLE XXVIII

<u>DAYS OF STORAGE</u>	<u>% FOSTHIAZATE REMAINING ON CARRIER</u>			
	<u>AGSORB CN</u> <u>0.05% Ni</u>	<u>PEANUTSHELL</u> <u>0.025% Cu</u>	<u>PEANUTSHELL</u> <u>0.025% Ni</u>	<u>PUMICE</u> <u>STONE</u>
0	10.3	8.6	9.2	9.0
60	10.0	9.9	10.1	9.6
150	9.7	9.9	11.2	10.4

EXAMPLE 41

Same as Example 5, except that the Fosthiazate impregnated carriers were stored at 45°C. Table XXIX below shows that at a higher temperature, slight reduction in the assay of Fosthiazate may occur. However, this reduction of assay is not related to the transition metal ions.

TABLE XXIX

<u>DAYS OF STORAGE</u>	<u>% FOSTHIAZATE REMAINING ON CARRIER</u>			
	<u>AGSORB CN</u> <u>0.05% Ni</u>	<u>PEANUTSHELL</u> <u>0.025% Cu</u>	<u>PEANUTSHELL</u> <u>0.025% Ni</u>	<u>PUMICE</u> <u>STONE</u>
0	10.3	8.6	9.2	9.0
6	9.4	9.2	8.6	9.9
60	9.1	8.7	8.1	8.0
150	7.2	8.8	8.6	10.3

EXAMPLE 42

Four Agsorb CN carriers were impregnated with 0.05%, 0.10%, 0.20% and 0.25% CuSO₄, respectively. The carriers were then impregnated with Fosthiazate and stored at different temperatures for different amounts of time to evaluate the effect of CuSO₄ concentration on Fosthiazate stability. Table XXX shows that the carrier impregnated with 0.20% CuSO₄ gave the best stability.

TABLE XXX

<u>DAYS/TEMP.</u> <u>OF STORAGE</u>	<u>% FOSTHIAZATE REMAINING ON CARRIER</u>			
	<u>0.05% CuSO₄</u>	<u>0.10% CuSO₄</u>	<u>0.20% CuSO₄</u>	<u>0.25% CuSO₄</u>
3 Days/25°C	10.6	10.5	10.5	10.4
3 Days/45°C	10.7	10.8	10.9	10.8
11 Days/45°C	10.2	10.4	10.2	10.4
28 Days/45°C	10.2	10.3	10.2	10.1

EXAMPLE 43

A porous container filled with a charcoal carrier impregnated with 0.15% CuSO₄, was placed within a container containing Fosthiazate 10G to evaluate the effect of the Cu/Charcoal deodorizer on the stability of the Fosthiazate.

The container was stored for 1 month at room temperature. Table XXXI below shows that the stability was unaffected by the Cu/Charcoal deodorizer.

TABLE XXXI

<u>SAMPLE</u>	<u>% FOSTHIAZATE REMAINING</u>
Fosthiazate 10G	9.4
Fosthiazate 10G + 0.15% Cu/Charcoal	9.5

The composition of the present invention is useful with any composition that contains a sulfur-containing organic compound. While specific examples of sulfur-containing organic compounds were illustrated above, those in the art will appreciate that other materials containing sulfur-containing organic compounds can be substituted for those shown above.

Having described the invention in detail and by reference to the preferred embodiments and example thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.

What is claimed is:

1. A method for reducing the odor associated with a formulation containing a sulfur-containing organic compound which comprises associating a polyvalent transition metal compound with a malodorous sulfur-containing organic compound such that odor is reduced.
2. The method of claim 1 wherein the transition metal compound is selected from a group consisting of copper, nickel, iron, zinc compounds and combinations thereof.
3. The method of claim 3 wherein the transition metal compound is selected from a group consisting of copper, nickel, iron, zinc compounds and combinations thereof.
4. The method of claim 1 wherein the transition metal compound is present on a carrier.
5. The method of claim 4 wherein the transition metal compound is admixed with the sulfur-containing organic compound.
6. The method of claim 5 wherein the sulfur-containing organic compound is co-present on the carrier with the transition metal compound.
7. The method of claim 1 wherein the formulation is a liquid and the transition metal compound is dissolved or dispersed in the liquid.
8. The method of claim 1 wherein the transition metal compound is packaged separately from said formulation in a porous compartment.
9. The method of claim 8 wherein the porous compartment is present within a container containing the formulation such that the transition metal compound is physically isolated from, but in gaseous communication with, the formulation.

10. A composition which comprises a sulfur-containing organic compound in admixture with a polyvalent transition metal compound, the transition metal compound being present in an amount sufficient to reduce the odor of the sulfur-containing organic compound.

11. The composition of claim 10 wherein the transition metal compound is selected from a group consisting of copper, nickel, iron, zinc compounds and combinations thereof.

12. The composition of claim 11 wherein the transition metal compound is selected from a group consisting of copper, nickel, iron, zinc salts and combinations thereof.

13. The composition of claim 12 wherein the transition metal compound is present on an inert carrier.

14. The composition of claim 13 wherein the inert carrier is selected from a group consisting of clay granules, ground peanut hull, lava pumice stone, granulated gypsum, synthetic aluminum silicate, and precipitated silica.

15. The composition of claim 13 wherein the transition metal compound is present on the carrier in an amount in the range from about 0.01 to 15% dry weight based on the dry weight of the carrier.

16. The composition of claim 15 wherein the polyvalent transition metal compound is a copper salt.

17. The composition of claim 16 wherein the copper salt is present on the carrier in an amount of about 0.05% to 12.0% by weight based on the weight of the carrier.

18. The composition of claim 13 wherein the sulfur-containing organic compound is co-present on the carrier with the transition metal compound.

19. The composition of claim 18 wherein the sulfur-containing organic compound is an agricultural chemical.
20. The composition of claim 19 wherein the agricultural chemical formulation is selected from a group consisting of Fosthiazate, methylene-bis-thiocyanate, Chlormephos and Chlorpyrifos.
21. A container for a liquid or powder formulation containing a sulfur-containing organic compound which exhibits an odor, the container including a compartment therein retaining a polyvalent transition metal compound separate from, but in gaseous communication with, the sulfur-containing organic compound such that the odor of the sulfur-containing organic compound is reduced.
22. The container of claim 21 wherein the compartment is porous.
23. The container of claim 22 wherein the compartment is selected from a group consisting of filter bags, perforated cap inserts and long semi-permeable tubes.
24. The container of claim 21 wherein the transition metal compound is present on a carrier.
25. The container of claim 24 wherein the carrier is selected from a group consisting of activated charcoal, granular charcoal, powder kaolinite clays, granulated silica gel, powder silica and gypsum, clay granules, ground peanut hull, lava pumice stone, granulated gypsum, synthetic aluminum silicate, precipitated silica, recycled paper, ground corncob and mullite.
26. The container of claim 24 wherein the transition metal compound is present on the carrier in an amount in the range from about 0.1 to 15% by weight of carrier.

27. The container of claim 3 wherein the polyvalent transition metal compound is a copper salt.
28. The container of claim 27 wherein the copper salt is about 0.1% by weight to about 15% by weight of the carrier.
29. The container of claim 21 wherein the sulfur-containing organic compound is an agricultural chemical formulation.
30. The container of claim 29 wherein the agricultural chemical formulation is selected from a group consisting of Fosthiazate, Methylene-bis-thiocyanate, Chlormephos and Chlorpyrifos.
31. The composition of claim 8 wherein said composition is a liquid and said transition metal compound is dissolved or dispersed in the composition.
32. The composition of claim 31 wherein the composition further contains a surfactant.

[received by the International Bureau on 07 May 1997 (07.05.97);
original claims 3, 27 and 31 amended;
remaining claims unchanged (2 pages)]

1. A method for reducing the odor associated with a formulation containing a sulfur-containing organic compound which comprises associating a polyvalent transition metal compound with a malodorous sulfur-containing organic compound such that odor is reduced.
2. The method of claim 1 wherein the transition metal compound is selected from a group consisting of copper, nickel, iron, zinc compounds and combinations thereof.
3. The method of claim 2 wherein the transition metal compound is selected from a group consisting of copper, nickel, iron, zinc salts and combinations thereof.
4. The method of claim 1 wherein the transition metal compound is present on a carrier.
5. The method of claim 4 wherein the transition metal compound is admixed with the sulfur-containing organic compound.
6. The method of claim 5 wherein the sulfur-containing organic compound is co-present on the carrier with the transition metal compound.
7. The method of claim 1 wherein the formulation is a liquid and the transition metal compound is dissolved or dispersed in the liquid.
8. The method of claim 1 wherein the transition metal compound is packaged separately from said formulation in a porous compartment.
9. The method of claim 8 wherein the porous compartment is present within a container containing the formulation such that the transition metal compound is physically isolated from, but in gaseous communication with, the formulation.

27. The container of claim 21 wherein the polyvalent transition metal compound is a copper salt.
28. The container of claim 27 wherein the copper salt is about 0.1% by weight to about 15% by weight of the carrier.
29. The container of claim 21 wherein the sulfur-containing organic compound is an agricultural chemical formulation.
30. The container of claim 29 wherein the agricultural chemical formulation is selected from a group consisting of Fosthiazate, Methylene-bis-thiocyanate, Chlormephos and Chlorpyrifos.
31. The composition of claim 10 wherein said composition is a liquid and said transition metal compound is dissolved or dispersed in the composition.
32. The composition of claim 31 wherein the composition further contains a surfactant.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/00089

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A61L 9/00

US CL : 422/5; 424/421; 423/244.06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 422/1, 5; 424/421; 423/244.06; 210/638, 644

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, CAPLUS

search terms: sulfur, odor, copper sulfate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,494,481 A (RODRIGUEZ ET AL) 22 January 1985 (22.01.85), see entire document.	1-6, 10-18 ----- 4-6, 13-18, 24- 26, 31, 32
Y	US 5,346,068 A (GOUGE ET AL) 13 September 1994 (13.09.94), see column 1, lines 9-12, column 3, lines 20-23, and column 6, line 40.	19, 20, 29, 30

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A		document defining the general state of the art which is not considered to be of particular relevance
* E		earlier document published on or after the international filing date
* L		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
* O		document referring to an oral disclosure, use, exhibition or other means
* P		document published prior to the international filing date but later than the priority date claimed
	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
	* A	document member of the same patent family

Date of the actual completion of the international search

07 APRIL 1997

Date of mailing of the international search report

30 APR 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

LEIGH DAWSON

Telephone No. (703) 306-0651

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/00089

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 5,458,848 A (BURGAUD) 17 October 1995 (17.10.95), see entire document.	1-3,7-12, 21-23,27 <hr/> 4-6,13-20, 24-26,28, 31,32

Form PCT/ISA/210 (continuation of second sheet)(July 1992)*

**CORRECTED
VERSION***

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: A61L 9/00	A1	(11) International Publication Number: WO 97/25076 (43) International Publication Date: 17 July 1997 (17.07.97)
(21) International Application Number: PCT/US97/00089 (22) International Filing Date: 3 January 1997 (03.01.97) (30) Priority Data: 60/009,898 11 January 1996 (11.01.96) US 08/604,665 21 February 1996 (21.02.96) US (71) Applicant: ISK BIOSCIENCES CORPORATION [US/US]; 5966 Heisley Road, P.O. Box 8000, Mentor, OH 44061 (US). (72) Inventors: RAYTHATHA, Rasik, Haridas; 3618 Spring Arbor Way, Kingwood, TX 77345 (US). FOWLER, Randy, Eugene; 801 Briargreen Street, Pasadena, TX 77503 (US). (74) Agents: LEVY, Mark, P. et al.; 2000 Courthouse Plaza, N.E., P.O. Box 8801, Dayton, OH 45401-8801 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>With amended claims.</i>
(54) Title: ODOR CONTROL FOR COMPOSITIONS CONTAINING ORGANIC SULFUR COMPOUNDS (57) Abstract. A method and composition for controlling and reducing the odor of odoriferous components and/or by-products of formulations containing sulfur-containing organic compounds using a transition metal compound; the polyvalent transition metal compound is preferably provided on a carrier.		

* (Referred to in PCT Gazette No. 46/1997, Section II)

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**ODOR CONTROL FOR COMPOSITIONS
CONTAINING ORGANIC SULFUR COMPOUNDS**

This application is claims the benefit of provisional application Ser. No. 60/009,898 filed Jan. 11, 1996.

Background of the Invention

The present invention relates to a method for controlling the odor of sulfur-containing organic compounds, such as nematicides and other pesticides, more particularly, this invention relates to a method for controlling the odor of sulfur-containing organic compounds using a polyvalent transition metal compound.

Agricultural compositions often include active agents which are sulfur-containing organic compounds which frequently exhibit odor. In many cases, the odor results from by-products and other impurities, such as low molecular weight mercaptans which are formed in the course of manufacturing the compounds. A number of approaches have been taken to controlling the odor of agricultural chemical formulations. Some of these approaches rely upon masking the odors with fragrances others have relied upon expensive methods, such as encapsulation. In general prior approaches have met with only limited success.

Japanese Patent No. 55/041846 to Furuya et al. discloses an adsorption process using activated charcoal impregnated with copper sulfate to remove the odorant, hydrogen sulfide, from a waste gas. Czechoslovakia Patent No. 175003 to Brych et al. teaches impregnation of common sorbents, such as activated charcoal, with metal salts to give a sorbent which traps ammonia, hydrogen sulfide and potassium cyanate gases at high relative humidity (greater than 75%). Japanese Patent No. 52/108388 to Hamaguchi discloses the treatment of activated charcoal-sodium pellets with metal ions for gas treatment or deodorization.

Adsorption by an activated charcoal carrier impregnated with a metal ion is not always an effective

approach to odor control because pesticides, such as Fosthiazate, bind to the activated charcoal so tenaciously that the Fosthiazate is not released and it is rendered nonfunctional as a pesticide.

Accordingly, there is a need for effective and cost efficient techniques for controlling and reducing the odor of sulfur-containing organic compounds, such as pesticides.

Summary of the Invention

It has been found that polyvalent transition metal compounds are useful in controlling and reducing the odor associated with sulfur-containing organic compounds. This finding is especially useful in controlling and reducing the odor of agricultural chemicals, such as pesticides. While the exact mechanism by which the transition metal compounds control the odor of the odoriferous components and by-products of the sulfur-containing organic compounds is not clear, the transition metal ions have been observed to complex with sulfur and it is believed that this complexation reaction may be functional in reducing odor in accordance with the present invention. The transition metal ions may complex with the odoriferous components and by-products. The transition metal ions may catalyze a reaction which decomposes the odoriferous components and by-products without affecting the stability of the sulfur-containing active agent. Furthermore, it is believed that the reaction is catalytic rather than adsorptive in nature because the odor control appears to endure indefinitely which suggests that the transition metal is not consumed in the reaction.

In accordance with one embodiment of the invention, the transition metal compound is simply added to a formulation containing a sulfur-containing organic compound. For example, a transition metal compound can be added neat to a solution or dispersion of an agricultural chemical which exhibits an odor problem. It does not appear to matter whether the transition metal compound dissolves in the formulation or not. The

transition metal compound has been observed to be capable of reducing odor if it dissolves in the formulation or if it simply resides as a sediment in the formulation.

The transition metal compound can also be dry mixed with a dry powder formulation and work effectively. While the transition metal compound can be used neat, it is preferred to adsorb or absorb or imbibe the transition metal compound onto an inert carrier. Where the formulation is a dry powder, a carrier containing the transition metal compound can be blended with the powder containing the active agent. In some cases, the active agent has been co-deposited on the carrier with the transition metal compound.

In summary, one manifestation of the present invention is for controlling the odor of odoriferous components and by-products of sulfur-containing organic compounds, such as nematicides and other pesticides, wherein a transition metal compound is added to the formulation containing the organic sulfur-containing compound.

Another manifestation of the invention is a composition useful in controlling the odor of sulfur-containing compounds which comprises a transition metal compound on a carrier and a sulfur-containing organic compound. In one particular embodiment of the invention, the composition comprises an inert carrier, a polyvalent transition metal compound and a sulfur-containing organic compound, such as a nematicide or other pesticide co-deposited on the carrier.

In another embodiment of the invention, the composition is a liquid formulation containing a sulfur-containing organic compound in which a polyvalent transition metal compound is dissolved or dispersed in the formulation.

In yet another embodiment of the invention, a container for a sulfur-containing organic compound which exhibits odor is provided wherein the container includes a compartment therein for retaining a polyvalent transition metal compound separate from, but in deodorizing communication with the sulfur-containing organic compound such that the odor

of the sulfur compound is reduced. The compartment is typically porous. Examples of porous elements that can be used with the invention are filter bags, perforated cap inserts, tubes of semi-permeable films, etc.

Still another embodiment of the invention is a carrier which is useful in controlling the odor of chemicals such as organic sulfur-containing compounds wherein the carrier has adsorbed or absorbed therein a transition metal compound.

Other objects and advantages of the present invention will be apparent from the following description and the appended claims.

Detailed Description

The use of polyvalent transition metal compounds in association with sulfur-containing organic compounds, such as nematicides and other pesticides, as described herein, provides unexpectedly good levels of odor control ranging from 24 hours to over one year. In addition to providing odor control, it has been observed that the polyvalent transition metal compounds provide enhanced stabilization of the active sulfur compounds in some cases. This stabilization has been observed using amounts less than is required for odor control. Throughout this disclosure, all references to sulfur containing organic compounds mean not only the active chemical but also the odoriferous components present with the active chemical to which the odor is generally attributed.

The polyvalent transition metal compound is preferably selected from a group consisting of copper, nickel, iron, zinc compounds and combinations thereof. Preferably, the polyvalent transition metal compound is a salt, such as a sulfate, nitrate or chloride. Representative examples of useful transition metal compounds include copper sulfate, nickel chloride, ferric chloride, zinc chloride, nickel sulfate, zinc sulfate, ferric sulfate and ferrous sulfate. More preferably, the salt is copper sulfate.

In accordance with the present invention, as previously noted, the transition metal compound can be associated with a sulfur-containing organic compound in various ways. In accordance with certain embodiments of the invention, the polyvalent transition metal compound is deposited onto an inert carrier. Any of a wide variety of inert carriers can be used for this purpose. Representative examples of useful carriers include clay granules, ground peanut hull, lava pumice stone, granulated gypsum, synthetic aluminum silicate, precipitated silica, activated charcoal, granular charcoal, powder kaolin clays, granulated silica gel, powder silica, recycled paper granule, ground corncob, mullite, synthetic porous silicates, calcined clays, etc. More preferably, the inert carrier is selected from a group consisting of clay granules, ground peanut hull, lava pumice stone, granulated gypsum, synthetic aluminum silicate and precipitated silica. The carrier preferably has an average particle size in the range of about 18 to 50 mesh and a liquid holding capacity of about 0.15 to 3.5 ml water per gram carrier. However, those skilled in the art will recognize that carriers having a larger or smaller particle size and a higher or lower liquid holding capacity will also be useful.

Typically, the transition metal compound will be deposited on the carrier in an amount of about 0.01 to 15 parts compound per 100 parts carrier. The amount of the compound that can be added to the carrier will vary with the nature of the compound, the nature of the carrier and its particle size. When copper sulfate is used, the copper sulfate is added to the carrier in an amount ranging from 0.05 to 12% by weight of carrier.

The carrier can be impregnated with the transition metal compound using an aqueous imbibition technique. The transition metal compound is typically dissolved in an amount of water equal to about 40 to 95% of the liquid holding capacity of the inert carrier. After the carrier has taken up the solution of the transition metal compound, the carrier is

dried in a conventional manner. One useful method for drying the carrier is to use a fluidized bed dryer.

The amount of the polyvalent transition metal compound blended with the active sulfur containing compound is a function of several factors including the nature of the formulation and the manner in which the transition metal compound is used with the formulation, e.g., whether it is admixed dry, dispersed in a liquid, adsorbed on a carrier, or containerized, as described herein in more detail. Generally, the transition metal compound is added to the organic sulfur containing compound in an amount of about 0.02 to about 0.4 parts by weight per 100 parts by weight of the organic sulfur-containing compound (inclusive of its odoriferous contaminants or byproducts).

It is believed that polyvalent transition metal compounds should be effective in controlling the odor of substantially any sulfur-containing organic compound and be widely applicable in the field of agricultural chemicals. It is believed that the chemical entities responsible for the odor of these compositions react with the transition metal compound as previously discussed.

The sulfur-containing organic compound of the present invention is preferably selected from a group consisting of agricultural chemicals, such as pesticides. Representative examples of the agricultural chemicals include Fosthiazate, Chlormephos, Chlorpyrifos, methylene-bis-thiocyanate, Furadan and Thimate. The sulfur-containing organic compound can be in a granular or dry powder form or dispersion form. One of the advantages of the invention is that the addition of the odor control agent typically does not require a major change in the established formulation of the active agent.

In one embodiment of the invention, the active agent can be co-deposited on a carrier with the transition metal compound. The amount of the sulfur-containing organic compound deposited on the carrier will be a function of the EPA standards which regulate the application rate of the

compound. To deposit the sulfur-containing compound on the carrier, the sulfur-containing organic compound is dissolved in a solvent and the solution is sprayed upon or imbibed into the carrier. Substantially any solvent in which the sulfur-containing organic compound is soluble, which is easily removed by drying, and which does not attack the carrier, should be suitable for this purpose. A solvent useful for Fosthiazate is methylene chloride. The concentration of the solution is easily adjusted for the liquid holding capacity of the carrier to provide a product having the desired amount of the active agent on the carrier which can be applied to crops or soil in a conventional manner. The amounts of transition metal compound and sulfur-containing compound will be adjusted to provide the desired deodorizing effect. Generally, the transition metal compound is effective in relatively small amounts. Higher amounts can be used, provided that the amount of transition metal compound does not destabilize the active compound too greatly. Preferably, the transition metal compound is present in an amount of about 0.02 to 0.4 parts of the transition metal compound per 100 parts of the organic sulfur-containing compound as previously stated. For this embodiment wherein the transition metal compound and the active agent are co-deposited on the carrier, the transition metal compound is usually added to the carrier in an amount of about -0.025 to 0.25 parts by weight based on 100 parts by dry weight of the carrier alone.

In another embodiment, the composition is an admixture of a carrier containing a polyvalent transition metal compound and a dry powder formulation containing a sulfur-containing organic compound. In this embodiment, the transition metal compound is separately present on the carrier and mixed with the active compound in the amounts which have previously discussed.

In another embodiment, the composition is a liquid formulation containing the sulfur-containing organic compound in which a polyvalent transition metal compound is dissolved or dispersed. It is desirable that a surfactant is added to

the liquid formulation. The surfactant facilitates the blending of the formulation and the transition metal compound. Preferably, the transition metal compound is present in the liquid formulation in an amount ranging from about 0.2 to 14 parts by weight per 100 parts by weight of the organic sulfur containing compound.

Yet another embodiment of the present invention is a container for a liquid or powder formulation containing a sulfur-containing organic compound in which a compartment is provided for separately retaining a polyvalent transition metal compound. There must be vaporous communication between the compartment containing the transition metal compound and the formulation containing the sulfur compound. By associating the porous container containing the transition metal compound in proximity to the sulfur-containing organic compounds in this manner, the odoriferous components and by-products of the sulfur-containing organic compounds to come into contact with the transition metal compounds, thereby permitting deodorization. In this embodiment, the transition metal compound may be deposited onto a carrier in the same manner as described above or the compound may be used neat. The transition metal compound and carrier (optional) is then packaged in the compartment. The amount of transition metal compound that is packaged into the porous container is in the range from about 0.03 to 0.2 per 100 parts by weight of the organic sulfur containing compound.

Those skilled in the art will appreciate the diversity of materials that may be used to package the transition metal compound, such as a porous bag which may be paper or a microporous film formed into a bag which is simply added to the formulation, alternatively the transition metal compound can be housed in a cap or lid and separated from the formulation by a porous membrane of paper or film. A sponge member can be saturated with a solution of the transition metal compound, dried, and packaged with the formulation. The possible constructions are numerous.

The invention is illustrated in more detail by the following non-limiting examples.

In the following examples, odor is rated on a scale of 0 to 10, with 0 being no odor and 10 being extremely strong odor.

EXAMPLE 1

An inert carrier, 100 g granulated gypsum made by Agrisorbent Corporation (a division of Oil Dri Co.) with a maximum liquid holding capacity of 24 g of water/100 g of carrier, was impregnated with 0.2% by weight of copper sulfate pentahydrate supplied by Fisher Co., by dissolving 0.2 g of copper sulfate pentahydrate in 23 g of water and spraying this copper sulfate solution onto the carrier while gently mixing the granules. After all of the solution was added, the wet granules were mixed for 20 minutes using a device that tumbles granules with minimum shear force. The granules were then dried at 50°C in an oven for 8 hours. This pre-treated carrier was then treated with 10% of the sulfur-containing organic compound active ingredient, Fosthiazate. For loading, 8.93 g of carrier was used. 1.07 g of Fosthiazate was dissolved in 25 ml of methylene chloride. The solution of Fosthiazate was sprayed onto the carrier. Excessive amounts of methylene chloride were removed by vacuum evaporation.

EXAMPLE 2

The same carrier, polyvalent transition metal salt, active ingredient and method of preparing the carrier were used as in Example 1, except that the pre-treated carrier was loaded with Fosthiazate without using organic solvent. In this process Fosthiazate was sprayed directly on to carrier so there was no need to remove any solvent.

EXAMPLE 3

The type of carrier, transition metal compound and the method of impregnation were similar to Example 1.

However, the amount of transition metal compound was 0.05 g. Also, for final preparation 10.008 g of carrier impregnated with transition metal compound was used. In the process, 1.001 g of Fosthiazate was dissolved in 6 ml. of methylene chloride and added to the carrier. The rest of the process was similar to Example 1.

EXAMPLE 4

The type of carrier, transition metal compound and method of impregnation were similar to Example 1. However, the amount of transition metal compound was 0.05 g. Also, for final preparation 10.053 g of carrier impregnated with transition metal compound was used. In the process, 1.028 g Chlormephos was dissolved in 66.87 g of acetone and added to the carrier. The rest of the process was similar to Example 1.

EXAMPLE 5

The type of transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 1. However, the carrier was ground peanut-hull. The peanut-hull was ground to the size fraction between 18 to 30 mesh. The ground peanut-hull was dried overnight in an oven at 50°C. Separately, 0.026 g of transition metal compound was dissolved in 25.118 g of water and sprayed on to 12.48 g of the ground peanut-hull. The material was then dried overnight at 50°C to remove excessive moisture. The impregnation with Fosthiazate was carried out by dissolving 0.999 g of Fosthiazate in 6 ml. of methylene chloride. This solution was then added to 9.001 g of ground peanut-hull containing transition metal compound. The rest of the process was similar to Example 1.

EXAMPLE 6

The type of transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 1. However, the carrier was ground lava pumice stone from Guatemala. The carrier was in the size range of 12 to 35 mesh. As in Example 5, the carrier was dried overnight at 50°C. Separately, 0.078 g of transition metal compound was dissolved in 44.6 g of water, sprayed on to 100.2 g of the ground lava pumice stone, and dried overnight at 50°C. For Fosthiazate impregnation, the method and process were similar to Example 1.

EXAMPLE 7

The type of transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 1. However, the carrier was Synthetic Silica BXR 493 supplied by PPG Industries, Inc. The carrier was in the size range of 35 to 120 mesh. As in Example 5, the carrier was dried overnight at 50°C. Separately, 0.008 g of transition metal compound was dissolved in 102.3 g of water, sprayed on to 30.02 g of the carrier, and dried overnight at 50°C. For Fosthiazate impregnation, the method and process were similar to Example 1.

EXAMPLE 8

The type of transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 1. However, the carrier was Agsorb CN, manufactured by Agrisorbents (Group of Oil Dri). The carrier was in the size range of 24 to 48 mesh. As in Example 5, the carrier was dried overnight at 50°C. The amount of carrier used ranged from 100.000 g to 99.755 g. Various amounts of transition metal compound ranging from 0.000 g to 0.258 g was dissolved in 0 g to 20.003 g of water and sprayed on to the carrier. For Fosthiazate impregnation, the method and process were similar to Example 1.

EXAMPLE 9

A liquid formulation was prepared by dissolving 0.15 g copper sulfate in 161.67 g of water. To increase wetting and dispersing of the organic sulfur compound, 9.0 g of a surfactant was added to the liquid formulation. The organic sulfur compound, Methylene-bis-thiocyanate, was added to the formulation in an amount of 45.62 g. In addition, 45.62 g of another non-sulfurous active ingredient, Chlorothalonil, was also added to the formulation. This formulation was ground using a ball mill and its viscosity was adjusted. The resulting suspension concentrate had an odor rating of 3 compared to an odor rating of 10 for similar formulations prepared without copper sulfate.

EXAMPLE 10

A carrier, 10 g activated charcoal, was impregnated with a polyvalent transition metal compound, 10% by weight of carrier CuSO_4 . The pre-treated carrier was then packaged into a small filter bag in an amount of 0.3 g. This bag was then left in a container containing 10 g of a Fosthiazate formulation. Three observers were asked to rate severity of the odor on the scale of 0 to 10 where 0 indicates total odor control and 10 means no odor control. Use of the deodorizer gave odor control of 3 or less.

EXAMPLE 11

The type of polyvalent transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 10. However, the carrier was Kurry charcoal from Japan. The carrier was dried overnight at 50°C before using. 163.7 g of copper sulfate was dissolved in 950 g of water and sprayed on to 1200.2 g of dried Kurry charcoal. The resulting material was once again dried overnight at 50°C. 0.1 g, 0.2 g and 0.3 g of the resulting material was packaged in small micro-porous filter bags. These bags were then placed in containers containing 10 g of Fosthiazate 10G formulation. The odor was rated at regular intervals after

storage at ambient condition and at 45°C. Table I below shows that the copper sulfate impregnated Kurry charcoal produced a significant reduction in the odor. The results are based on an average of three observations.

TABLE I

COPPER KURRY CHAR- COAL	ODOR RATING AT AMBIENT CONDITIONS AND 45°C FOR DAYS											
	<u>2</u>		<u>3</u>		<u>6</u>		<u>17</u>		<u>38</u>		<u>48</u>	
	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>
0.0	10	10	10	10	10	10	10	10	10	10	10	10
0.1	1	1	1	1	2	2	0	0	2	1	0	1
0.2	1	0	1	0	1	1	0	0	0	1	1	1
0.3	0	0	0	1	0	1	0	0	0	1	0	1

EXAMPLE 12

The type of polyvalent transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 10. However, the carrier was calcined Kaolinite, Alphatex supplied by ECC America. The carrier was dried overnight at 50°C before using. 10 g of copper sulfate was dissolved in 45 g of water and sprayed on to 90 g of dried Alphatex. The resulting material was once again dried overnight at 50°C. 0.1 g, 0.2 g and 0.3 g of the resulting material was packaged in small micro-porous filter bags. These bags were placed in containers containing 10 g of Fosthiazate 10G formulation. The odor was rated at regular intervals after storage at ambient and at 45°C. Table II below shows that the copper sulfate impregnated Alphatex produced a significant reduction in the odor. The results are based on an average of three observations.

TABLE II

COPPER												
KURRY												
CHAR-												
COAL												
	<u>2</u>		<u>3</u>		<u>6</u>		<u>17</u>		<u>38</u>		<u>48</u>	
	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>	<u>AMB</u>	<u>45</u>
0.0	10	10	10	10	10	10	10	10	10	10	10	10
0.1	6	5	7	6	6	8	2	4	4	5	2	3
0.2	2	2	5	1	4	4	1	1	3	4	1	4
0.3	3	1	3	1	3	3	1	1	2	3	1	3

EXAMPLE 13

The type of polyvalent transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 10. However, the carrier was precipitated silica. The silica was precipitated by acidification of sodium silicate with sulfuric acid. The precipitated silica was washed thoroughly to remove adsorbed salt and dried in oven at 50°C. The material was ground and particles below 100 mesh were collected. 0.026 g of copper sulfate was dissolved in 6.013 g of water and sprayed on to 12.493 g of dried precipitated silica. The resulting material was then dried at 50°C for 24 hours to remove excess water. 0.023 g of nickel chloride was dissolved in 6.034 g of water and sprayed on to 12.494 g of dried precipitated silica. The resulting material was then dried at 50°C to remove excess water. Fosthiazate was impregnated on to these resulting materials as in Example 10. Table III below shows that copper sulfate and nickel chloride impregnated carriers produce a significant reduction in odor.

TABLE III

DEODORIZER ODOR RATING AT AMBIENT CONDITIONS OR 45°C.

	<u>2 DAYS @ AMB</u>	<u>6 MONTHS @ AMB</u>	<u>6 MONTHS @</u>
	<u>CONDITIONS</u>	<u>CONDITIONS</u>	<u>45°C</u>
None	10	10	10
Silica w/ copper	0	5	3
Silica w/ nickel	2	4	4

EXAMPLE 14

The type of polyvalent transition metal compound, active ingredient and method of impregnating the carrier were similar to Example 10. However, the carrier was dried Kurry charcoal. The amount of copper sulfate was in the range of 0.2 to 12% by weight of carrier. The amount of copper sulfate was varied as follows: 1) 163.7 g of copper sulfate was dissolved in 950 g of water and sprayed on to 1200.2 g of Kurry charcoal granules. The resulting material was dried overnight at 50°C. The resulting material had a copper sulfate loading of 11.95%; 2) for medium loading material, 18.05 g of copper sulfate was dissolved in 144.1 g of water and sprayed on to 182.02 g of Kurry charcoal. The resulting material was dried overnight at 50°C. The resulting material had a copper sulfate loading of 9.0%; 3) for lower loading material, 3.6 g of copper sulfate was dissolved in 960 g of water and sprayed on to 1200 g of Kurry charcoal. The resulting material was dried overnight at 50°C. The resulting material had a copper sulfate loading of 0.3%. 0.2 g of each of the resulting materials was packaged in micro-porous filter bags and placed with 20 g of Fosthiazate granules. The odor was rated after 24 hour day and one week. Table IV below shows that the loading percent of copper sulfate on to a carrier does not have a significant effect on the reduction in odor.

TABLE IV

LOADING OF COPPER SULFATE (%)	ODOR RATING	ODOR RATING
	@ 24 HOURS	@ 1 WEEK
0.3	1	2
9.0	1	1
11.95	1	1

EXAMPLE 15

The type of active ingredient and method of impregnating the carrier were similar to Example 10. However, the carrier was precipitated silica and the transition metal compounds were nickel chloride hexahydrate and ferric (III) chloride hexahydrate. 0.115 g of nickel chloride hexahydrate was dissolved in 9.6 g of water and sprayed on to 15 g of silica. The resulting material was dried at 50°C for 24 hours. 0.128 g of ferric (III) chloride hexahydrate was dissolved in 9.6 g of water and sprayed on to 15 g. of silica. The resulting material was dried at 50°C for 24 hours. 0.3 g of the resulting materials were packaged in filter bags and placed in contact with 50 g of Fosthiazate granules. The odor was rated after 2, 3 and 8 days. Table V below shows that the nickel chloride produced a more significant reduction in odor.

TABLE V

TRANSITION METAL COMPOUND	ODOR RATING		
	2 DAYS	5 DAYS	8 DAYS
Nickel chloride	1	1	0
Ferric chloride	3	2	1

EXAMPLE 18

The type of active ingredient and method of impregnating the carrier were similar to Example 10. However, the carriers for this study were precipitated silica and Kurry charcoal and the transition metal compounds were copper sulfate and nickel chloride. Both carriers were dried at 50°C for 24 hours before transition metal compound impregnation. 0.121 g. of copper sulfate pentahydrate was dissolved in 9.6 g of water and sprayed on to 15 g of dry silica. The resulting material was dried at 50°C for 24 hours. 0.115 g of nickel chloride hexahydrate was dissolved in 9.6 g of water and sprayed on to 15 g of dry silica. The resulting material was dried at 50°C for 24 hours. 3.6 g of copper sulfate was dissolved in 960 g of water and sprayed on to 1200 g of Kurry charcoal. The resulting material was dried overnight. The resulting material had a loading of 0.3% copper sulfate. 0.05 g of each resulting material was placed directly into contact with 2.0 g of Fosthiazate 75% EC. The odor was rated after 1, 24 and 144 hours. Table VI below shows that the nickel chloride generally produced a more significant reduction in odor.

TABLE VI

<u>CARRIER</u>	<u>ODOR RATING AFTER STORAGE FOR PERIOD OF TIME</u>		
	<u>1 HOUR</u>	<u>24 HOURS</u>	<u>144 HOURS</u>
Copper/Kurry	8	4	3
Copper/Silica	3	8	8
Nickel/Silica	6	3	3

EXAMPLE 19

The carrier was Agsorb S2100CN supplied by Agrisorbents (Oil Dri) Europe. The carrier was in the size range of 24 to 48 mesh. The carrier was dried overnight at 50°C. The transition metal compound is copper sulfate. 0.008 g of copper sulfate was dissolved in 7.2 g of water and

sprayed on to 30.0 g of Agsorb S2100CN. The resulting material was dried overnight at 50°C. For Fosthiazate impregnation method and process were similar to Example 1. The odor was rated after one week and one month of storage at 22°C and at 45°C. Table VII below shows that the copper sulfate on this carrier produced a significant reduction in odor. The results are based on an average of three observations.

TABLE VII

<u>CARRIER</u>	<u>% COPPER SULFATE</u>	<u>ODOR RATING AFTER 1 WEEK</u>		<u>ODOR RATING AFTER 1 MONTH</u>	
		<u>22°C</u>	<u>45°C</u>	<u>22°C</u>	<u>45°C</u>
Agsorb S2100CN	0.00	9	10	10	10
Agsorb S2100CN	0.025	1	2	1	1

EXAMPLE 20

The carrier was Biofix E2 supplied by ECC International. The carrier was in the size range of 24 to 48 mesh. The carrier was dried overnight at 50°C. The transition metal compound is copper sulfate. 0.008 g of copper sulfate was dissolved in 9.2 g of water and sprayed on to 30.022 g of Biofix E2. The resulting material was dried overnight at 50°C. For Fosthiazate impregnation method and process were similar to Example 1. The odor was rated after one week and one month of storage at 22°C and at 45°C. Table VIII below shows that the copper sulfate on this carrier produced a significant reduction in odor. The results are based on an average of three observations.

TABLE VIII

<u>CARRIER</u>	<u>% COPPER SULFATE</u>	<u>ODOR RATING AFTER</u> <u>1 WEEK</u>		<u>ODOR RATING AFTER</u> <u>1 MONTH</u>	
		<u>22°C</u>	<u>45°C</u>	<u>22°C</u>	<u>45°C</u>
Biofix E2	0.00	9	10	10	10
Biofix E2	0.025	2	1	2	2

EXAMPLE 21

The carrier was Illite clay granules supplied by Kentish Mineral. The carrier was in the size range of 18/40 mesh. The carrier was dried overnight at 50°C. The transition metal compound is copper sulfate. 0.008 g of copper sulfate was dissolved in 8.5 g of water and sprayed on to 30.004 g of Illite clay granules. The resulting material was dried overnight at 50°C. For Fosthiazate impregnation method and process were similar to Example 1. The odor was rated after one week and one month of storage at 22°C and at 45°C. Table IX below shows that the copper sulfate on this carrier produced a significant reduction in odor. The results are based on an average of three observations.

TABLE IX

<u>CARRIER</u>	<u>% COPPER SULFATE</u>	<u>ODOR RATING AFTER</u> <u>1 WEEK</u>		<u>ODOR RATING AFTER</u> <u>1 MONTH</u>	
		<u>22°C</u>	<u>45°C</u>	<u>22°C</u>	<u>45°C</u>
Illite 18/40	0.00	9	10	10	10
Illite 18/40	0.025	1	2	2	2

EXAMPLE 22

The carrier was Biodac (recycled paper) granules supplied by Edward Lowe Industry. The carrier was in the size range of 16/30 mesh. The carrier was dried overnight at 50°C. The transition metal compound is copper sulfate. 0.008 g of copper sulfate was dissolved in 13.6 g of water and sprayed on to 30.004 g of Biodac granules. The resulting material was dried overnight at 50°C. For Fosthiazate impregnation method and process were similar to Example 1. The odor was rated after one week and one month of storage at 22°C and at 45°C. Table X below shows that the copper sulfate on this carrier produced a significant reduction in odor. The results are based on an average of three observations.

TABLE X

<u>CARRIER</u>	<u>% COPPER SULFATE</u>	<u>ODOR RATING AFTER</u>		<u>ODOR RATING AFTER</u>	
		<u>1 WEEK</u>		<u>1 MONTH</u>	
		<u>22°C</u>	<u>45°C</u>	<u>22°C</u>	<u>45°C</u>
Biodac 16/30	0.00	9	10	10	10
Biodac 16/30	0.025	1	2	1	2

EXAMPLE 23

Four 10 g samples of Agsorb CN carrier supplied by Agrisorbents product group (A division of Oil Dri Corporation of America) were impregnated with 0.05%, 0.10%, 0.20% and 0.25% CuSO₄, respectively. The carriers were then impregnated with Fosthiazate and stored for 12 months at 22°C and 45°C. Fosthiazate impregnation was accomplished by dissolving 1.0 g of Fosthiazate in 6 ml. of methylene chloride. The resulting solution was blended with the carrier for 15 minutes. Volatile methylene chloride was removed by vacuum using Büchi rotovaporizer. The impregnated carriers were evaluated as to their odor compared with a 10 g Agsorb CN carrier impregnated with only Fosthiazate, no CuSO₄. Table XI below shows that the

odor rating of the carriers with CuSO_4 is substantially less than that of the carrier without CuSO_4 .

TABLE XI

<u>TEMP.</u>	<u>ODOR RATING</u>				
	0.0% <u>CuSO_4</u>	0.05% <u>CuSO_4</u>	0.10% <u>CuSO_4</u>	0.20% <u>CuSO_4</u>	0.25% <u>CuSO_4</u>
22°C	10	2	1	1	1
45°C	10	1	0	0	0

EXAMPLE 24

Two groups of four carriers were impregnated with Fosthiazate and stored for 6 months at 22°C and 45°C to evaluate the odor. The four carriers were: 1) Mexican pumice stone, 2) Mexican pumice stone impregnated with 0.05% CuSO_4 , 3) Guatemalan pumice stone, 4) Guatemalan pumice stone impregnated with 0.05% CuSO_4 . Table XII below shows that the odor rating of the carriers that were impregnated with CuSO_4 were substantially less than the carriers without CuSO_4 , especially at the storage temperature of 45°C.

TABLE XII

<u>STORAGE TEMP.</u>	<u>ODOR RATING</u>			
	<u>MEXICAN</u>	<u>MEXICAN/ CuSO_4</u>	<u>GUATEMALAN</u>	<u>GUATEMALAN/ CuSO_4</u>
22°C	2	2	6	2
45°C	8	1	6	1

EXAMPLE 25

Two groups of four Agsorb CN carriers were impregnated with Fosthiazate after being impregnated with different amounts of CuSO_4 to evaluate the effect of CuSO_4 concentration on odor. One group of impregnated carriers were stored for 55 days at room temperature and the other was stored for 55 days at 45°C. Table XIII below shows that the odor rating substantially decreases with the addition of CuSO_4 .

TABLE XIII

STORAGE 55 DAYS (TEMP.)	ODOR RATING				
	0.0%	0.05%	0.10%	0.20%	0.25%
	<u>CuSO_4</u>	<u>CuSO_4</u>	<u>CuSO_4</u>	<u>CuSO_4</u>	<u>CuSO_4</u>
R.T.	10.0	2.0	1.0	0.0	0.0
45°C	10.0	1.0	2.0	0.0	0.0

EXAMPLE 26

Two samples of 0.3 g of charcoal carrier were impregnated with CuSO_4 and then packaged into micro-porous filter bags (similar to tea bags) and stowed inside perforated bottle caps. The bottle caps were then used to close containers containing Fosthiazate. The combinations were stored at room temperature and at 45°C for various periods to evaluate the effect of charcoal impregnated with CuSO_4 on the odor rating. Table XIV below shows that there is an immediate decrease in the odor and a continued odor controlling effect.

TABLE XIV

<u>DAYS OF STORAGE</u>	<u>ODOR RATING</u>	
	<u>AT ROOM TEMP.</u>	<u>AT 45°C</u>
0	10	10
1	1	1
2	0	0
3	0	1
5	0	1
18	0	0
48	0	1
116	0	1

EXAMPLE 27

Six different types of deodorizers were placed within containers containing Fosthiazate 75% EC. The deodorizers were in direct contact with the Fosthiazate. The containers were stored at room temperature for various lengths of time. The amount of deodorizer packaged into the porous container was varied. Table XV below shows that carriers impregnated with polyvalent transition metal compounds gave the best odor control, even at lower concentrations. However, Cu/Silica was not very effective for longer periods.

TABLE XV

<u>DEODORIZER</u>	<u>PERCENT DEODORIZER</u>	<u>ODOR RATING AT ROOM TEMPERATURE</u>			
		<u>1 HR</u>	<u>24 HRS</u>	<u>30 DAYS</u>	<u>5 MONTHS</u>
None	0.0	10.0	10.0	10.0	10.0
Epoleon N-100	1.0	10.0	10.0	10.0	10.0
Epoleon NnZ	1.0	10.0	10.0	10.0	10.0
Epoleon N7C	1.0	10.0	10.0	10.0	10.0
Cu/Charcoal	0.5	8.0	4.0	2.0	N/A
Cu/Silica	0.5	3.0	8.0	8.0	8.0
Ni/Silica	0.5	6.0	3.0	2.0	2.0

EXAMPLE 28

A comparison of the types of odor eliminators was conducted. The control was no odor eliminator. The odor eliminators were charcoal, 0.3 g charcoal impregnated with copper and 0.3 g clay impregnated with copper. The deodorizers were packaged into micro-porous filter bags placed directly over 20.0 g of Fosthiazate granules contained within a container and stored for 14 days at room temperature and at 45°C and for 439 days at room temperature and at 45°C. The odor control of each type of deodorizer was evaluated. Table XVI below shows that the charcoal impregnated with copper gave the best odor control.

TABLE XVI

STORAGE DAYS AT TEMP.	ODOR RATING			
	<u>CONTROL</u>	<u>CHARCOAL</u>	<u>Cu/CHARCOAL</u>	<u>Cu/CLAY</u>
14 Days/ Room Temp.	10	3	0	1
14 Days/ 45°C	10	4	0	1
439 Days/ Room Temp.	10	6	1	1
439 Days/ 45°C	10	7	0	1

EXAMPLE 29

A comparison of the types of odor eliminators was conducted. The control was no odor eliminator. The odor eliminators were charcoal, charcoal impregnated with copper and clay impregnated with copper. 0.1 g of each deodorizer was packaged into a micro-filter bags placed directly over 20.0 g of Fosthiazate granules contained within a container and stored at room temperature for various days. The odor control of each deodorizer was evaluated. Table XVII below shows that the activated charcoal impregnated with copper gave the best odor control. Clay impregnated with copper was less effective at controlling odor. Activated charcoal was only partially effective in controlling odor over a 120 day period.

TABLE XVII

<u>DAYS OF STORAGE</u>	<u>ODOR RATING</u>			
	<u>CONTROL</u>	<u>CHARCOAL</u>	<u>Cu/CHARCOAL</u>	<u>Cu/CLAY</u>
0	10	10	10	10
1	10	8	2	7
5	10	5	1	6
10	10	4	2	6
20	10	6	0	2
50	10	8	0	2
110	10	8	1	3
440	10	8	1	4

EXAMPLE 30

Various amounts of charcoal impregnated with copper were packaged into micro-porous filter bags and placed directly over 20 g of Fosthiazate 10G granules contained within a container. The containers were stored for various lengths of time at room temperature to evaluate the effect of deodorizer concentration on odor control. Table XVIII below shows that all the amounts of Cu/Charcoal were effective in controlling odor.

TABLE XVIII

<u>DAYS OF STORAGE</u>	<u>ODOR RATING AT VARIOUS AMOUNTS OF DEODORIZER</u>			
	<u>0.0 g</u>	<u>0.1 g</u>	<u>0.2 g</u>	<u>0.3 g</u>
0	10	10	10	10
5	10	1	1	0
10	10	1	1	0
20	10	0	0	0
440	10	1	1	1

EXAMPLE 31

A comparison of the types of odor eliminators was conducted. The control was no odor eliminator. The odor eliminators were charcoal, charcoal impregnated with copper and clay impregnated with copper. 0.1 g of each deodorizer was packaged into micro-porous filter bags and placed directly over 20.0 g of Fosthiazate granules contained within a container and stored at 45°C for various days. Table XIX below shows that the charcoal impregnated with copper gave the best odor control.

TABLE XIX

<u>DAYS OF STORAGE</u>	<u>ODOR RATING</u>			
	<u>CONTROL</u>	<u>CHARCOAL</u>	<u>Cu/CHARCOAL</u>	<u>Cu/CLAY</u>
0	10	10	10	10
1	10	8	2	6
2	10	6	1	5
4	10	5	0	6
6	10	6	1	8
18	10	7	0	4
45	10	5	1	3
116	10	6	3	5

EXAMPLE 32

0.3 g and 0.6 g of charcoal carrier were impregnated with copper and packaged into micro-porous filter bags and placed directly over various amounts of Fosthiazate granules contained within containers and stored for 370 days at room temperature and 45°C to evaluate the effect of the amount of Fosthiazate on the odor control of the carrier. The control was no deodorizer. Table XX below shows that the amount of Fosthiazate does not significantly alter the odor controlling properties of the carriers, especially when a larger amount of carrier is used.

TABLE XX

STORAGE TEMP. AND <u>DEODORIZER</u>		ODOR RATING BASED ON AMOUNT OF <u>FOSTHIAZATE IN GRAMS</u>				
		<u>50</u>	<u>95</u>	<u>145</u>	<u>295</u>	<u>395</u>
ROOM TEMP.	Control	10	10	10	10	10
	0.3 g	1	3	4	5	5
	Cu/Charcoal					
	0.6 g	0	2	2	4	2
	Cu/Charcoal					
45°C	Control	10	10	10	10	10
	0.3 g	3	3	3	5	7
	Cu/Charcoal					
	0.6 g	3	2	3	3	3
	Cu/Charcoal					

EXAMPLE 33

Various amounts of charcoal impregnated with copper were packaged into micro-porous filter bags and placed directly over 20 g of Fosthiazate 10G contained within containers. The containers were stored for various lengths of time at room temperature to evaluate the effect of deodorizer concentration on odor control. Table XXI below shows that all the amounts of Cu/Charcoal were effective in controlling odor.

TABLE XXI

<u>DAYS OF STORAGE</u>	<u>ODOR RATING AT VARIOUS AMOUNTS OF DEODORIZER</u>			
	<u>0.0 g</u>	<u>0.1 g</u>	<u>0.2 g</u>	<u>0.3 g</u>
0	10	10	10	10
1	10	1	1	0
2	10	1	1	0
7	10	1	1	0
14	10	0	0	0

EXAMPLE 34

0.3 g and 0.6 g of charcoal carrier were impregnated with copper and packaged into micro-porous filter bags and placed directly over various amounts of Fosthiazate granules contained within containers and stored for 8 days at room temperature to evaluate the effect of the amount of Fosthiazate on the odor control of the carrier. The control was no deodorizer. Table XXII below shows that the impregnated carriers were effective for a wide range of amounts of Fosthiazate.

TABLE XXII

<u>CARRIER</u>	<u>ODOR RATING BASED ON AMOUNT OF FOSTHIAZATE IN GRAMS</u>				
	<u>50</u>	<u>95</u>	<u>145</u>	<u>295</u>	<u>395</u>
Control	10	10	10	10	10
0.3 g Cu/Charcoal	2	3	4	6	8
0.6 g Cu/Charcoal	1	1	1	2	2

EXAMPLE 35

25 g emulsifiable concentrate of Fosthiazate was contained in a container with a cap that housed a compartment filled with 1.0% charcoal carrier impregnated with copper to evaluate the odor controlling effect of the Cu/Charcoal. Table XXIII below shows that the Cu/Charcoal significantly reduces the odor of the emulsifiable concentrate.

TABLE XXIII

STORAGE <u>DAYS</u>	<u>ODOR RATING</u>	
	<u>75% EC (CONTROL)</u>	<u>75% EC + 1.0% Cu/CHARCOAL</u>
0	10	10
7	10	5
22	10	3
34	10	3

In addition to the odor control, the polyvalent transition metal compounds also enhance the stability of the sulfur-containing organic compounds impregnated into a polyvalent transition metal compound treated carrier. Several tests which follow were completed to support this finding.

EXAMPLE 36

Two Fosthiazate impregnated carriers were prepared. The first carrier, acidic peanutshell, was impregnated only with the Fosthiazate. The second carrier, acidic peanutshell, was impregnated first with CuSO₄ and then with Fosthiazate. Table XXIV below shows the results of the study that evaluated the stability of Fosthiazate. The stability of Fosthiazate is significantly enhanced when a carrier is pre-treated with a polyvalent transition metal compound.

TABLE XXIV

<u>TIME AND TEMP.</u>	<u>% FOSTHIAZATE ON ACIDIC PEANUTSHELL</u>	<u>% FOSTHIAZATE ON COPPER/PEANUTSHELL</u>
Initial	9.90	10.1
One week @ 45°C	9.60	N/A
One month @ 45°C	3.50	N/A
2 months @ Rm.Temp	N/A	10.0
2 months @ 45°C	N/A	9.40

EXAMPLE 37

Four Fosthiazate impregnated carriers were prepared and stored at 22°C for 0 to 180 days to evaluate the percent of Fosthiazate remaining in the carriers. The first carrier was Mexican pumice stone. The second carrier was Mexican pumice stone impregnated with 0.05% by weight carrier CuSO_4 . The third carrier was Guatemalan pumice stone. The fourth carrier was Guatemalan pumice stone impregnated with 0.05% by weight carrier CuSO_4 . Table XXV below shows that only a minute percent of Fosthiazate is lost during the 180 days of storage.

TABLE XXV

<u>DAYS OF STORAGE</u>	<u>% FOSTHIAZATE REMAINING ON CARRIER</u>			
	<u>MEXICAN CARRIER</u>	<u>MEXICAN & CuSO₄</u>	<u>GUATEMALAN CARRIER</u>	<u>GUATEMALAN & CuSO₄</u>
0	9.8	9.9	10.5	11.3
60	9.6	10.6	11.1	11.4
180	9.7	9.6	10.5	11.3

EXAMPLE 38

Four 10G Agsorb CN carriers were impregnated with 0.05%, 0.10%, 0.20% and 0.25% CuSO_4 , respectively. The carriers were then impregnated with 10.3% Fosthiazate and stored for 370 days to evaluate the effect of CuSO_4 concentration on the stability of the Fosthiazate. Table XXVI

below shows that lower concentrations of CuSO₄ stabilize the Fosthiazate better than higher concentrations.

TABLE XXVI

<u>DAYS OF STORAGE</u>	<u>% FOSTHIAZATE REMAINING ON CARRIER</u>			
	<u>0.05% CuSO₄</u>	<u>0.10% CuSO₄</u>	<u>0.20% CuSO₄</u>	<u>0.25% CuSO₄</u>
0	10.5	10.5	10.5	10.5
50	9.6	10.0	10.0	10.0
180	10.3	11.0	10.2	9.8
370	10.2	9.8	9.6	6.0

EXAMPLE 39

Two groups of four different types of carriers were impregnated with 0.025% CuSO₄ and different amounts of Fosthiazate and stored for 6 weeks at 22°C and 43°C to evaluate the effect of various carriers on stability. The carriers were: Agsorb CN, Mexican pumice stone, Guatemalan pumice stone, and Costa Rica pumice stone. Table XXVII below shows that the Guatemalan pumice stone carrier gave the best stability.

TABLE XXVII

<u>WEEKS & STORAGE TEMP.</u>	<u>% FOSTHIAZATE REMAINING ON CARRIER</u>			
	<u>AGSORB CN</u>	<u>MEXICAN</u>	<u>GUATEMALAN</u>	<u>COSTA RICA</u>
Initial	10.8	8.8	8.2	9.5
6 Wks/22°C	10.1	9.4	10.8	9.3
6 Wks/43°C	9.3	8.1	11.5	8.5

EXAMPLE 40

An Agsorb CN carrier was impregnated with 0.05% nickel ion. Two peanutshell carriers were impregnated with 0.025% copper ion and 0.025% nickel ion, respectively. A pumice stone carrier was not impregnated with a metal ion. All the carriers were impregnated with Fosthiazate and stored at 22°C for up to 150 days to evaluate the effect of carriers and metal ions on the stability of Fosthiazate. Table XXVIII below shows that peanutshell carrier impregnated with nickel ion stabilized the Fosthiazate the best after 150 days of storage.

TABLE XXVIII

<u>DAYS OF STORAGE</u>	<u>% FOSTHIAZATE REMAINING ON CARRIER</u>			
	<u>AGSORB CN</u> <u>0.05% Ni</u>	<u>PEANUTSHELL</u> <u>0.025% Cu</u>	<u>PEANUTSHELL</u> <u>0.025% Ni</u>	<u>PUMICE</u> <u>STONE</u>
0	10.3	8.6	9.2	9.0
60	10.0	9.9	10.1	9.6
150	9.7	9.9	11.2	10.4

EXAMPLE 41

Same as Example 5, except that the Fosthiazate impregnated carriers were stored at 45°C. Table XXIX below shows that at a higher temperature, slight reduction in the assay of Fosthiazate may occur. However, this reduction of assay is not related to the transition metal ions.

TABLE XXIX

<u>DAYS OF STORAGE</u>	<u>% FOSTHIAZATE REMAINING ON CARRIER</u>			
	<u>AGSORB CN</u> <u>0.05% Ni</u>	<u>PEANUTSHELL</u> <u>0.025% Cu</u>	<u>PEANUTSHELL</u> <u>0.025% Ni</u>	<u>PUMICE</u> <u>STONE</u>
0	10.3	8.6	9.2	9.0
6	9.4	9.2	8.6	9.9
60	9.1	8.7	8.1	8.0
150	7.2	8.8	8.6	10.3

EXAMPLE 42

Four Agsorb CN carriers were impregnated with 0.05%, 0.10%, 0.20% and 0.25% CuSO₄, respectively. The carriers were then impregnated with Fosthiazate and stored at different temperatures for different amounts of time to evaluate the effect of CuSO₄ concentration on Fosthiazate stability. Table XXX shows that the carrier impregnated with 0.20% CuSO₄ gave the best stability.

TABLE XXX

<u>DAYS/TEMP.</u> <u>OF STORAGE</u>	<u>% FOSTHIAZATE REMAINING ON CARRIER</u>			
	<u>0.05% CuSO₄</u>	<u>0.10% CuSO₄</u>	<u>0.20% CuSO₄</u>	<u>0.25% CuSO₄</u>
3 Days/25°C	10.6	10.5	10.5	10.4
3 Days/45°C	10.7	10.8	10.9	10.8
11 Days/45°C	10.2	10.4	10.2	10.4
28 Days/45°C	10.2	10.3	10.2	10.1

EXAMPLE 43

A porous container filled with a charcoal carrier impregnated with 0.15% CuSO₄, was placed within a container containing Fosthiazate 10G to evaluate the effect of the Cu/Charcoal deodorizer on the stability of the Fosthiazate.

The container was stored for 1 month at room temperature. Table XXXI below shows that the stability was unaffected by the Cu/Charcoal deodorizer.

TABLE XXXI

<u>SAMPLE</u>	<u>% FOSTHIAZATE REMAINING</u>
Fosthiazate 10G	9.4
Fosthiazate 10G + 0.15% Cu/Charcoal	9.5

The composition of the present invention is useful with any composition that contains a sulfur-containing organic compound. While specific examples of sulfur-containing organic compounds were illustrated above, those in the art will appreciate that other materials containing sulfur-containing organic compounds can be substituted for those shown above.

Having described the invention in detail and by reference to the preferred embodiments and example thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.

What is claimed is:

1. A method for reducing the odor associated with a formulation containing a sulfur-containing organic compound which comprises associating a polyvalent transition metal compound with a malodorous sulfur-containing organic compound such that odor is reduced.
2. The method of claim 1 wherein the transition metal compound is selected from a group consisting of copper, nickel, iron, zinc compounds and combinations thereof.
3. The method of claim 3 wherein the transition metal compound is selected from a group consisting of copper, nickel, iron, zinc compounds and combinations thereof.
4. The method of claim 1 wherein the transition metal compound is present on a carrier.
5. The method of claim 4 wherein the transition metal compound is admixed with the sulfur-containing organic compound.
6. The method of claim 5 wherein the sulfur-containing organic compound is co-present on the carrier with the transition metal compound.
7. The method of claim 1 wherein the formulation is a liquid and the transition metal compound is dissolved or dispersed in the liquid.
8. The method of claim 1 wherein the transition metal compound is packaged separately from said formulation in a porous compartment.
9. The method of claim 8 wherein the porous compartment is present within a container containing the formulation such that the transition metal compound is physically isolated from, but in gaseous communication with, the formulation.

10. A composition which comprises a sulfur-containing organic compound in admixture with a polyvalent transition metal compound, the transition metal compound being present in an amount sufficient to reduce the odor of the sulfur-containing organic compound.
11. The composition of claim 10 wherein the transition metal compound is selected from a group consisting of copper, nickel, iron, zinc compounds and combinations thereof.
12. The composition of claim 11 wherein the transition metal compound is selected from a group consisting of copper, nickel, iron, zinc salts and combinations thereof.
13. The composition of claim 12 wherein the transition metal compound is present on an inert carrier.
14. The composition of claim 13 wherein the inert carrier is selected from a group consisting of clay granules, ground peanut hull, lava pumice stone, granulated gypsum, synthetic aluminum silicate, and precipitated silica.
15. The composition of claim 13 wherein the transition metal compound is present on the carrier in an amount in the range from about 0.01 to 15% dry weight based on the dry weight of the carrier.
16. The composition of claim 15 wherein the polyvalent transition metal compound is a copper salt.
17. The composition of claim 16 wherein the copper salt is present on the carrier in an amount of about 0.05% to 12.0% by weight based on the weight of the carrier.
18. The composition of claim 13 wherein the sulfur-containing organic compound is co-present on the carrier with the transition metal compound.

19. The composition of claim 18 wherein the sulfur-containing organic compound is an agricultural chemical.
20. The composition of claim 19 wherein the agricultural chemical formulation is selected from a group consisting of Fosthiazate, methylene-bis-thiocyanate, Chlormephos and Chlorpyrifos.
21. A container for a liquid or powder formulation containing a sulfur-containing organic compound which exhibits an odor, the container including a compartment therein retaining a polyvalent transition metal compound separate from, but in gaseous communication with, the sulfur-containing organic compound such that the odor of the sulfur-containing organic compound is reduced.
22. The container of claim 21 wherein the compartment is porous.
23. The container of claim 22 wherein the compartment is selected from a group consisting of filter bags, perforated cap inserts and long semi-permeable tubes.
24. The container of claim 21 wherein the transition metal compound is present on a carrier.
25. The container of claim 24 wherein the carrier is selected from a group consisting of activated charcoal, granular charcoal, powder kaolinite clays, granulated silica gel, powder silica and gypsum, clay granules, ground peanut hull, lava pumice stone, granulated gypsum, synthetic aluminum silicate, precipitated silica, recycled paper, ground corncob and mullite.
26. The container of claim 24 wherein the transition metal compound is present on the carrier in an amount in the range from about 0.1 to 15% by weight of carrier.

27. The container of claim 3 wherein the polyvalent transition metal compound is a copper salt.
28. The container of claim 27 wherein the copper salt is about 0.1% by weight to about 15% by weight of the carrier.
29. The container of claim 21 wherein the sulfur-containing organic compound is an agricultural chemical formulation.
30. The container of claim 29 wherein the agricultural chemical formulation is selected from a group consisting of Fosthiazate, Methylene-bis-thiocyanate, Chlormephos and Chlorpyrifos.
31. The composition of claim 8 wherein said composition is a liquid and said transition metal compound is dissolved or dispersed in the composition.
32. The composition of claim 31 wherein the composition further contains a surfactant.

[received by the International Bureau on 07 May 1997 (07.05.97);
original claims 3, 27 and 31 amended;
remaining claims unchanged (2 pages)]

1. A method for reducing the odor associated with a formulation containing a sulfur-containing organic compound which comprises associating a polyvalent transition metal compound with a malodorous sulfur-containing organic compound such that odor is reduced.
2. The method of claim 1 wherein the transition metal compound is selected from a group consisting of copper, nickel, iron, zinc compounds and combinations thereof.
3. The method of claim 2 wherein the transition metal compound is selected from a group consisting of copper, nickel, iron, zinc salts and combinations thereof.
4. The method of claim 1 wherein the transition metal compound is present on a carrier.
5. The method of claim 4 wherein the transition metal compound is admixed with the sulfur-containing organic compound.
6. The method of claim 5 wherein the sulfur-containing organic compound is co-present on the carrier with the transition metal compound.
7. The method of claim 1 wherein the formulation is a liquid and the transition metal compound is dissolved or dispersed in the liquid.
8. The method of claim 1 wherein the transition metal compound is packaged separately from said formulation in a porous compartment.
9. The method of claim 8 wherein the porous compartment is present within a container containing the formulation such that the transition metal compound is physically isolated from, but in gaseous communication with, the formulation.

27. The container of claim 21 wherein the polyvalent transition metal compound is a copper salt.
28. The container of claim 27 wherein the copper salt is about 0.1% by weight to about 15% by weight of the carrier.
29. The container of claim 21 wherein the sulfur-containing organic compound is an agricultural chemical formulation.
30. The container of claim 29 wherein the agricultural chemical formulation is selected from a group consisting of Fosthiazate, Methylene-bis-thiocyanate, Chlormephos and Chlorpyrifos.
31. The composition of claim 10 wherein said composition is a liquid and said transition metal compound is dissolved or dispersed in the composition.
32. The composition of claim 31 wherein the composition further contains a surfactant.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/00089

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : A61L 9/00 US CL : 422/5; 424/421; 423/244.06 According to International Patent Classification (IPC) or to both national classification and IPC																				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 422/1, 5; 424/421; 423/244.06; 210/638, 644 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS, CAPLUS search terms: sulfur, odor, copper sulfate																				
C. DOCUMENTS CONSIDERED TO BE RELEVANT																				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																		
X --- Y	US 4,494,481 A (RODRIGUEZ ET AL) 22 January 1985 (22.01.85), see entire document.	1-6, 10-18 ----- 4-6, 13-18, 24-26, 31, 32																		
Y	US 5,346,068 A (GOUGE ET AL) 13 September 1994 (13.09.94), see column 1, lines 9-12, column 3, lines 20-23, and column 6, line 40.	19, 20, 29, 30																		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.																				
<table border="0"><tr><td>* Special categories of cited documents:</td><td>T</td><td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td></tr><tr><td>*A* document defining the general state of the art which is not considered to be of particular relevance</td><td>X*</td><td>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td></tr><tr><td>*E* earlier document published on or after the international filing date</td><td>Y*</td><td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td></tr><tr><td>*L* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td><td>A*</td><td>document member of the same patent family</td></tr><tr><td>*O* document referring to an oral disclosure, use, exhibition or other means</td><td></td><td></td></tr><tr><td>*P* document published prior to the international filing date but later than the priority date claimed</td><td></td><td></td></tr></table>			* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	*A* document defining the general state of the art which is not considered to be of particular relevance	X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	*E* earlier document published on or after the international filing date	Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	*L* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	A*	document member of the same patent family	*O* document referring to an oral disclosure, use, exhibition or other means			*P* document published prior to the international filing date but later than the priority date claimed		
* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention																		
A document defining the general state of the art which is not considered to be of particular relevance	X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone																		
E earlier document published on or after the international filing date	Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																		
L document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	A*	document member of the same patent family																		
O document referring to an oral disclosure, use, exhibition or other means																				
P document published prior to the international filing date but later than the priority date claimed																				
Date of the actual completion of the international search 07 APRIL 1997		Date of mailing of the international search report 30 APR 1997																		
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer LEIGH DAWSON Telephone No. (703) 306-0651																		

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/00089

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 5,458,848 A (BURGAUD) 17 October 1995 (17.10.95), see entire document.	1-3, 7-12, 21-23, 27 <hr/> 4-6, 13-20, 24-26, 28, 31, 32

Form PCT/ISA/210 (continuation of second sheet)(July 1992)*

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)